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AN EXPERIMENTAL STUDY OF OIL SPILL TREATING AGENTS THAT INHIBIT EMULSIFICATION AND PROMOTE DISPERSION

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AN EXPERIMENTAL STUDY OF OIL SPILL TREATING AGENTS THAT INHIBIT EMULSIFICATION AND PROMOTE DISPERSION

by

S.L. Ross Environmental Research Limited
Ottawa, Ontario

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AN EXPERIMENTAL STUDY OF OIL SPILL TREATING AGENTS THAT INHIBIT EMULSIFICATION AND PROMOTE DISPERSION

prepared by

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for the

Environmental Emergencies Technology Division
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Ottawa, Ontario

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ABSTRACT

As a result of extensive bench-scale, small-scale and meso-scale testing a new type of oil spill control chemical has been identified. The product, Brand "S", is a surfactant which both inhibits the formation of water-in-oil emulsions and promotes natural dispersion of oil slicks. The chemical is effective in preventing emulsification at dosages as low as one part inhibitor to 20,000 parts oil with fresh crude oil at 20°C. Increasing oil viscosity (either through decreasing temperature or oil weathering) requires higher doses, up to 1:1,000 at 0°C for fresh oil.

At dosages on the order of 1:1,000 at temperatures higher than 10°C the chemical also results in significant, rapid dispersion of the slick.

Four regimes of emulsion prevention have been identified. First, with no inhibitor present, the oil (unless 20°C below its pour point) rapidly incorporates water to form a stable, highly viscous brown emulsion (a "mousse"). Second at certain low concentrations of inhibitor, the oil still emulsifies but the emulsion is black coloured and the entrained water droplets are larger and the water content, viscosity and stability of the emulsion are lower than with the inhibitor-free oil. Third, at higher inhibitor concentrations, emulsification is prevented and the oil remains fluid. At this stage dispersed oil concentrations are higher than for the untreated oil. Finally, at still higher inhibitor concentrations the oil is completely dispersed into the water in the form of very small droplets.

An oil slick, dosed with the appropriate concentration of inhibitor, will, over long periods, do one of two things, either it will rapidly disperse or not emulsify and disperse more slowly, but at a rate much faster than untreated emulsion. In either case the effect is advantageous from the perspective of spill cleanup and impact.

RÉSUMÉ

Un autre type de produit chimique utilisable pour le nettoyage des déversements de pétrole a été reconnu à la suite de tests poussés, effectués à l'échelle laboratoire, de même qu'à petite et moyenne échelle. Le produit en question, Brand "S", est un surfactant qui à la fois inhibe la formation d'émulsions eau dans l'huile et favorise la dispersion naturelle des nappes de pétrole. Il empêche efficacement l'émulsification à des doses aussi faibles qu'une partie pour 20 000 parties de pétrole brut "frais", à 20 °C. L'accroissement de la viscosité (causé soit par la diminution de la température ou le vieillissement de la nappe) augmente les doses requises, jusqu'à 1:1000, à 0 °C, pour le pétrole frais.

A des doses de l'ordre de 1:1000 et à une température supérieure à 10 °C, le produit entraîne également une dispersion importante et rapide de la nappe.

On a déterminé quatre régimes de prévention de l'émulsification. Premièrement, en l'absence d'inhibiteur, le pétrole (à moins que sa température ne soit de 20 °C au-dessous de son point d'écoulement) incorpore rapidement l'eau pour former une émulsion stable, fortement visqueuse, de couleur brune (une "mousse"). Deuxièmement, à des concentrations peu élevées de l'inhibiteur, le pétrole forme encore une émulsion, mais celle-ci est de couleur noire, et les gouttelettes d'eau entraînées sont plus grosses; de plus, la teneur en eau, la viscosité et la stabilité de l'émulsion sont plus faibles. Troisièmement, à des concentrations plus élevées de l'inhibiteur, l'émulsification est empêchée, et le pétrole reste fluide. Dans ce cas, les concentrations du pétrole dispersé sont plus élevées que pour une nappe non traitée. Enfin, à des concentrations encore plus élevées, le pétrole est complètement dispersé dans l'eau où il se retrouve sous forme de très petites gouttelettes.

Lorsqu'une nappe de pétrole est traitée avec la concentration appropriée de l'inhibiteur, elle pourra, sur une longue période, soit se disperser rapidement, soit s'émulsifier et se disperser plus lentement, quoique plus rapidement que sans traitement. Dans un cas comme dans l'autre, l'effet est avantageux du point du vue du nettoyage et des répercussions.

TABLE OF CONTENTS

		Page
	ABSTRACT	i
	RESUME	ii
	LIST OF FIGURES	vii
	LIST OF TABLES	xii
	LIST OF PLATES	xiv
	FOREWORD	xv
	ACKNOWLEDGEMENTS	xvi
1.0	INTRODUCTION	1
1.1	Statement of Problem	1
1.1.1	Spreading and Weathering	
1.1.2	Fast Response Needed	1
1.1.3	Helping Nature Gradually Disperse the Oil	2
1.2	Dispersion vs. Emulsification	3
1.2.1	Natural Dispersion	3
1.2.2	Evaporation	4
1.2.3	Water-in-Oil Emulsification	5
1.2.4	Treating Emulsions	11
1.3	Summary of Problem	14
1.4	Objective of the Study	15
1.5	Study Approach	15

TABLE OF CONTENTS (Cont.)

		Page
2.0	PRELIMINARY SCREENING AND BENCH-SCALE TESTING OF SURFACTANTS	17
2.1	Purpose	17
2.2	Methods	17
2.2.1	Test Procedure	17
2.2.2	Test Oils	19
2.2.3	The Surfactants	20
2.3	Results and Discussion	20
2.4	Summary and Conclusions	31
3.0	SMALL-SCALE EFFECTIVENESS TESTING	32
3.1	Purpose	32
3.2	Methods	32
3.2.1	Apparatus	32
3.2.2	Test Matrix	32
3.2.3	Experimental Procedure	34
3.3	Results and Discussion	37
3.3.1	Emulsification and Dispersion of Fresh Oil	38
3.3.2	Effects of Oil Weathering on Surfactant Performance	44
3.3.3	Effects of Temperature on Surfactant Performance	48
3.3.4	Combined Effect of Weathering and Temperature	51
3.3.5	Effect of Slick Thickness on Surfactant Performance	55
3.3.6	Effect of Mixing Energy on Surfactant Performance	55

TABLE OF CONTENTS (Cont.)

		Page
3.3.7	Surfactant Application Techniques	60
3.3.8	Comparison with Dispersants	60
3.4	Summary and Conclusions	68
4.0	DISPERSANT EFFECTIVENESS TESTING	70
4.1	Purpose	70
4.2	Methods	70
4.3	Results and Discussion	71
4.4	Summary and Conclusions	80
5.0	MESO-SCALE EFFECTIVENESS TESTS	81
5.1	Purpose	81
5.2	Methods	81
5.3	Results and Discussion	83
5.4	Summary and Conclusions	92
6.0	MODELLING	96
6.1	Purpose	96
6.2	Theory	96
6.2.1	Emulsification	96
6.2.2	Dispersion	99
6.2.3	Linking the Models	100
6.2.4	Rate Constant Expressions	101
6.2.4.1	K^1_F and K_F	101
6.2.4.2	F_O and F_W	102
6.2.4.3	K^1_{LR} and K^1_{SR}	103
6.2.4.4	K_{LS} and K_{SS}	103
6.2.4.5	K_{SC}	103

TABLE OF CONTENTS (Cont.)

		Page
6.2.5	Property Changes	105
6.2.5.1	Viscosity	105
6.2.5.2	Interfacial Tension	105
6.3	Model Results	106
7.0	CONCLUSIONS AND RECOMMENDATIONS	109
7.1	Conclusions	109
7.2	Recommendations	110
8.0	REFERENCES	111
	APPENDIX I - COMPUTER PROGRAM LISTING	113

LIST OF FIGURES

Figure No.		Page
1	Computed and Experimental Viscosities versus Volume Fraction Evaporated (Bow River)	6
2	Computed and Experimental Viscosity versus Volume Fraction Evaporated (Sour Blend)	7
3	Photomicrograph of a water-in-oil emulsion	8
4	Stylized sketch showing polar molecules that make up film around water droplets	8
5	Photomicrograph of water droplet in water-in-oil emulsion	8
6	Photomicrograph of water-in-oil emulsion showing two water droplets touching but unable to merge because of film around droplets	8
7	Viscosity versus Water Content of Emulsion	9
8	Photomicrograph of single water droplet in untreated water	13
9	Two samples of the same water-in-oil emulsion maintained at the same temperature over a number of days	13

LIST OF FIGURES (Cont.)

Figure No.		Page
10	Emulsification versus Time (Fresh J-34 at 20°C)	39
11	Dispersion versus Time (Fresh J-34 at 20°C)	41
12	Emulsification versus Time (Fresh J-34 at 20°C)	42
13	Dispersion versus Time (Fresh ASMB at 20°C)	43
14	Effect of Weathering on Surfactant Performance: Emulsification versus Time (J-34 at 20°C)	45
15	Effect of Weathering on Surfactant Performance: Dispersion versus Time (J-34 at 20°C)	46
16	Effect of Weathering on Surfactant Performance: Emulsification versus Time (ASMB at 20°C)	47
17	Effect of Weathering on Surfactant Performance: Dispersion versus Time (ASMB at 20°C)	49
18	Effect of Temperature on Surfactant Performance: Emulsification versus Time (J-34)	50
19	Effect of Temperature on Surfactant Performance: Dispersion versus Time (J-34)	52
20	Effect of Slick Thickness on Surfactant Performance: Emulsification versus Time (Fresh J-34 at 20°C)	56

LIST OF FIGURES (Cont.)

Figure No.		Page
21	Effect of Slick Thickness on Surfactant Performance: Dispersion versus Time (Fresh J-34 at 20°C)	57
22	Effect of Mixing Energy on Surfactant Performance: Emulsification versus Time (Fresh J-34 at 20°C)	58
23	Effect of Mixing Energy on Surfactant Performance: Dispersion versus Time (Fresh J-34 at 20°C)	59
24	Comparison of Surfactant Application Methods: Emulsification versus Time (J-34 at 20°C)	61
25	Comparison of Surfactant Application Methods: Dispersion versus Time (J-34 at 20°C)	62
26	Comparison of Surfactant Application Methods: Dispersion versus Time (ASMB at 20°C)	63
27	Comparison of Surfactants: Emulsification versus Time (J-34 at 20°C)	64
28	Comparison of Surfactants: Dispersion versus Time (J-34 at 20°C)	65
29	Effect of Water Salinity on Surfactant Performance: Emulsification versus Time (Fresh J-34 at 20°C)	66

LIST OF FIGURES (Cont.)

Figure No.		Page
30	Effect of Water Salinity on Surfactant Performance: Dispersion versus Time (Fresh J-34 at 20°C)	67
31	Effectiveness of Brand S as a Dispersant at 15°C	73
32	Effectiveness of Brand S as a Dispersant at 20°C	74
33	Dispersant Effectiveness of Brand S at E:O= 1:500 as a Function of Temperature	76
34	Comparison of Temperature Effects on Dispersant Effectiveness	77
35	Emulsification Versus Time (J-34)	85
36	Emulsification versus Time (J-34)	87
37	Emulsification versus Time (J-34)	89
38	Emulsification versus Time (J-34)	90
39	Emulsification versus Time (ASMB)	91
40	Dispersion versus Time (ASMB)	93
41	Emulsification versus Time	94

LIST OF FIGURES (Cont.)

Figure No.		Page
42	Schematic of Model Processes	97
43	Model Results - Emulsification versus Time	107
44	Model Results - Dispersion versus Time	108

LIST OF TABLES

Table No.		Page
1	Consequences of emulsification of oil with time	9
2	Relative Emulsifying Tendencies of Crude Oils	10
3	Weathered Oil Characteristics	19
4	A Summary of Surfactant Performance J-34 Crude Oil at 20°C	22
5	A Summary of Surfactant Performance Kuwait Oil at 20°C	23
6	A Summary of Surfactant Performance J-34 Crude Oil at 10°C	24
7	A Summary of Surfactant Performance Kuwait Oil at 10°C	25
8	A Summary of Surfactant Performance J-34 Crude Oil at 1°C	26
9	A Summary of Surfactant Performance Kuwait Oil at 1°C	27
10	Quantitative Performance of Brand "S" in Salt Water	29
11	Properties of Surfactants	30
12	Physical Properties of the Alberta Sweet Mixed Blend Crude Oil	35

LIST OF TABLES (Cont.)

Table No.		Page
13	Physical Properties of the Avalon J-34 Crude Oil	36
14	Effects of Temperature on Surfactant Performance: ASMB	53
15	A Summary of the Lowest Feasible Concentration of Brand S Required to Inhibit Emulsification Under Various Conditions	54
16	Dispersant Effectiveness of Brand "S"	72
17	Effectiveness of Corexit 9527 and Brand "S" Combined	78
18	Effectiveness of Corexit 9550 and Brand "S" Combined	79
19	Summary of Wind/Wave Tank Trials	84

LIST OF PLATES

Plate No.		Page
1	Burrell Wrist-Action Shaker	18
2	An Example of Fully Recovered Oil	18
3	An Example of a Water-in-Oil Emulsion	18
4	Hoop Tank Apparatus	33
5	Wind/Wave Tank	82

FOREWORD

This study was conducted by Dr. S.L. Ross and Mr. I.A. Buist of S.L. Ross Environmental Research Limited under contract to Environment Canada. Mr. M. Fingas, of the Environmental Emergencies Technology Division, Environmental Protection Service, was Scientific Authority for the study.

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1.0 INTRODUCTION

1.1 STATEMENT OF PROBLEM

1.1.1 Spreading and Weathering

The two most undesirable properties of large offshore oil spills affecting cleanup at sea are the spreading characteristics of the oil slick and the tendency of the oil to become viscous through weathering processes. Spreading occurs rapidly so that a response using spill containment devices is usually not feasible. Dispersants are often not practical because total application time is much greater than "weathering" time (days vs hours), and currently available chemicals are not effective on viscous oil slicks.

1.1.2 Fast Response Needed

One solution is to decrease the spill response time before extensive spreading and weathering occur. In the case of tanker accidents, the tanker itself could be used for responding to the spill. Countermeasures equipment would be stored on-board and, in the event of a spill, would be immediately deployed before the slick became too large or too viscous. This concept was fully explored in a recent study for Environment Canada entitled "On-Board Self-Help Systems for Arctic Tankers" (S. L. Ross 1983).

Unfortunately the study concluded that conventional countermeasures approaches of containment/recovery and chemical dispersion are generally not feasible, especially for very large spills. The main problem is that a large stockpile of specialized equipment or materials would be needed to deal with the spill, and these would have to be efficiently utilized within a reasonable amount of time. Although a sufficient quantity of booms and skimmers could be stored on board a large oil tanker, their deployment

would be highly inefficient considering the difficulty of operating from the substantial freeboard, and the general problems of manipulating the control equipment once on the high seas, especially without the use of workboats.

The effective use of dispersants was rejected for other reasons, one of which was the enormous quantities of chemical that would have to be uneconomically stockpiled on the vessel. For example, to deal with a 10,000 m^3 spill, about 1000 m^3 of dispersant and at least one helicopter with application gear would be required. Only about 1 m^3 of dispersant could be applied per helicopter sortie, and thus, about 1000 sorties would be needed to dose the entire oil slick. The time required for this operation is obviously much greater than that of the oil to weather to dispersant-resistant viscosities. It is worth noting, however, that if state-of-the-art dispersants were, say, 50 times more efficient so that only 20 m^3 of stockpiled material and 20 sorties were required, this could be considered a feasible approach. Unfortunately, the current expert opinion is that aerially-applied dispersants will never be dramatically more efficient than those already on the market or now in the final stages of development.

1.1.3 Helping Nature Gradually Disperse the Oil

It is clear from the above analysis that the instantaneous dispersion of a large batch oil spill through the application of chemical agents is often not a feasible countermeasures solution: both land-based and tanker self-help operations are too slow relative to weathering rates. It then becomes pertinent to ask whether chemical dispersion of an offshore spill should continue to be a realistic goal, and if it should, whether the dispersion must be instantaneous in nature. Certainly dispersion of marine spills is one of the most natural of oil spill processes, despite the adage that "oil and water don't mix". The turbulent seas that often cause marine accidents and spills, and

play havoc with spill recovery equipment, also mix oil into the water column without chemical assistance. Several historical offshore spills were almost completely dissipated in this way (e.g., Argo Merchant, Ekofisk, Burma Agate). It seems sensible to take advantage of this tremendous mixing force to deal with spills rather than trying to fight it using spill recovery systems. Also, the oil spill's tendency to spread accelerates the dispersion process and is generally unpreventable in any case.

The question then becomes: is it possible to add a very small quantity of chemical to a freshly discharged oil spill to ensure that it eventually disperses through natural mixing processes? If the answer is yes, then an on-board self-help system (or other systems) to apply the chemical might become feasible, as discussed above. Further, if the proportion of chemical required is particularly low, it might even be economical and practical to pre-mix the chemical into the oil prior to its transportation. This would avoid the difficult problem of applying the chemical onto the slick once formed.

1.2 DISPERSION VERSUS EMULSIFICATION

1.2.1 Natural Dispersion

Natural dispersion of oil slicks on the open sea is a poorly-understood phenomenon, but the major features of the process can be described based on general oil-water dispersion phenomena and recent studies specifically related to oil spill dispersion. (Audunson 1980, Buist 1979, Mackay et al 1980, Milgram et al 1978, Raj 1979).

An oil slick on the ocean surface is subject to wave-induced agitation which fragments and mixes the oil into the water. The resulting oil-in-water dispersion comprises of oil drops varying in size from large globules in the

centimetre range to small droplets in the micron range (10,000 μm = 1 cm). The large drops rise relatively quickly and coalesce on the surface reforming slicks; the very small droplets, whose rise velocities are negligible relative to diffusive eddy currents, are carried further into the water column and dilute to low concentrations. In summary, oil dispersion at sea is a continuous cyclical phenomenon in which (1) the slick is fragmented into drops of varying size; (2) the small drops dilute into the water; and (3) the large drops rise to the surface to re-start the cycle. The process whereby small droplets dilute into the water column is termed "natural dispersion".

It can be shown that as the sea state increases so does the percentage of dispersed oil containing the smaller oil droplets whose rise velocities are negligible compared to eddy diffusion velocities. There is an exponential relationship between sea state and oil-loss rate since an increase in wave energy not only breaks the oil into smaller droplets but also increases turbulent diffusion forces which maintain increasingly larger drops in the water column (that is, drops which would rise to the surface at lower sea states).

If the oil spill were undergoing no other chemical or physical changes, it is clear that eventually oil on the open sea would completely disperse. Even if only a very small fraction of the surface slick were broken into non-rising droplets during each disperse/resurface cycle, the oil slick would still gradually disappear after numerous cycles. The only case where this would not happen is perhaps for completely calm seas.

1.2.2 Evaporation

Unfortunately, a major physical process that occurs during, and works against, the dispersion process is evaporation. For thin crude oil slicks, evaporative losses in the range of 30-40 percent can occur in a matter of hours

and this increases the viscosity of the remaining oil, as shown in Figures 1 and 2. These curves for two typical crude oils show that the viscosity can increase approximately ten-fold over the entire exposure period. This adversely affects oil-in-water dispersion because the oil becomes increasingly more difficult to shear or fragment. Nevertheless, it is water-in-oil emulsification and not evaporation by itself that is the primary process which increases oil viscosity and negatively affects the dispersion process.

1.2.3 Water-in-Oil Emulsification

Oil spill emulsification is more poorly understood than dispersion although recent work at the University of Toronto on behalf of Environment Canada is advancing knowledge in some key areas. Excellent literature reviews on the subject are available in Payne and Phillips 1985 and Mackay and Zagorski 1982.

A water-in-oil emulsion ("chocolate mousse") is a highly viscous oil spill product composed of up to about 80 percent water and 20 percent oil. The water is in the form of micron-sized droplets dispersed and tightly bound in a continuous phase of oil (see Figures 3 to 6). Table 1 and Figure 7 show that emulsions can have viscosities one hundred or more times greater than the parent oil. It is obvious that, once a surface oil spill is converted into a stable, viscous emulsion, its chances of being broken up and dispersed by wave action are greatly reduced. Almost all crude oils in the world tend to form emulsions, and as shown in Table 2, some are more stable than others. Many of the world's major crude oil tanker spills and blowouts resulted in the formation of stable emulsions and these stayed on the water surface and eventually were driven onto shorelines (Torrey Canyon, Ixtoc 1, Amoco Cadiz, etc.).

It is reasonable to speculate that emulsions physically form in a manner similar to oil-in-water dispersions, except that oil and not water is the continuous phase of the oil/water mixture. The process might be described as follows:

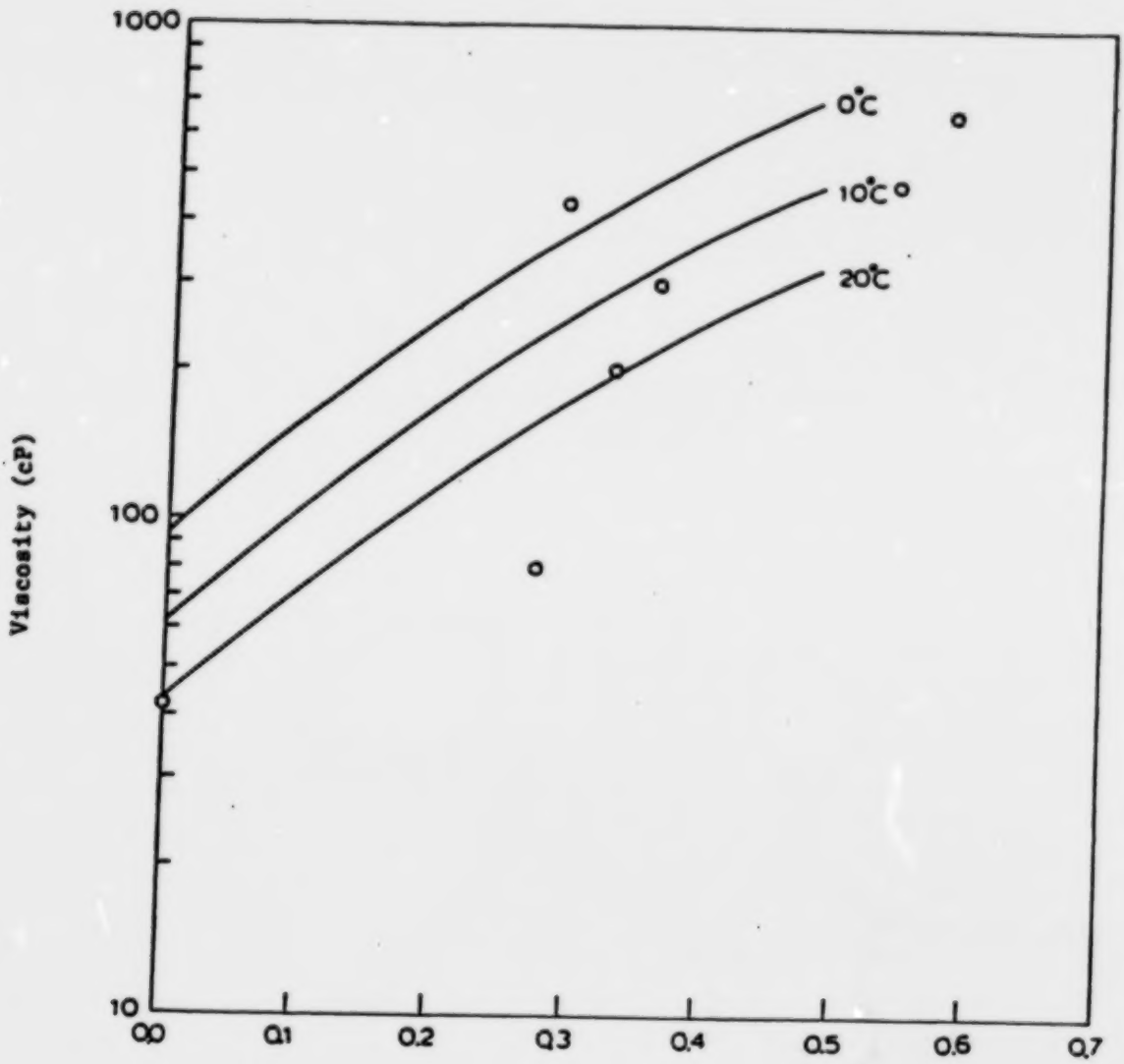


Figure 1 Computed and Experimental Viscosities versus Volume Fraction Evaporated. (Bow River)

(from Mackay,1980)

(from Mackay.1980)

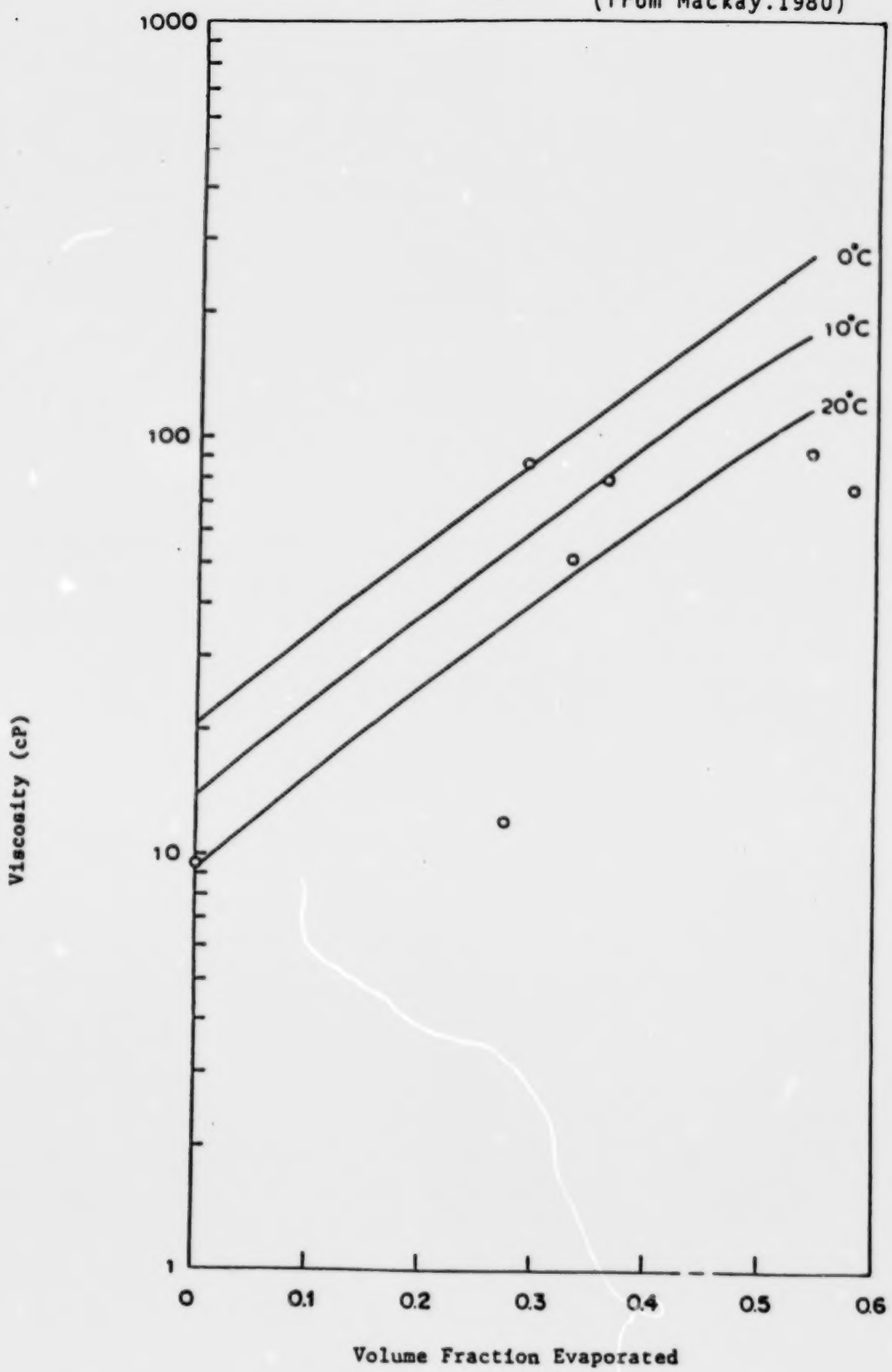


Figure 2 Computed and Experimental Viscosities versus Volume Fraction Evaporated. (Sour Blend)

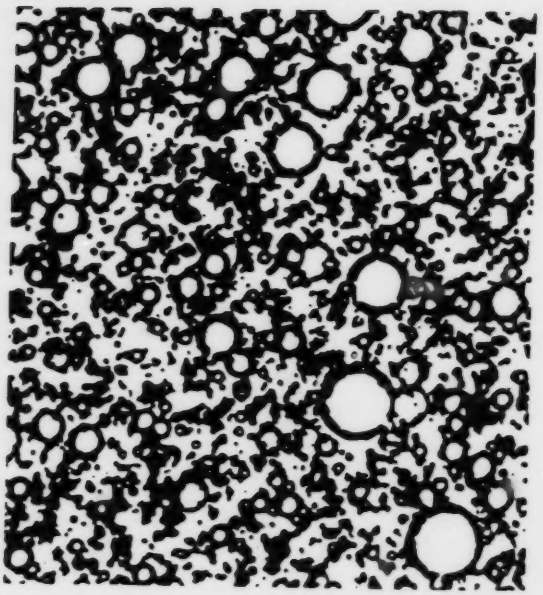


Figure 3 Photomicrograph of a water-in-oil emulsion. The clear circles are water droplets dispersed in oil. Note that droplets are of all different sizes.

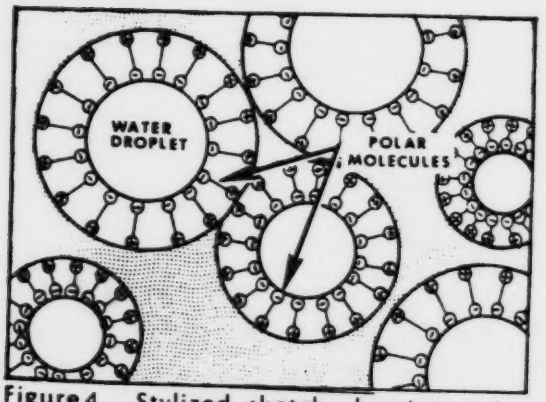


Figure 4 Stylized sketch showing polar molecules that make up film around water droplets. Each molecule has a positive and a negative end.

Figure 5 Photomicrograph of water droplet in water-in-oil emulsion. Note that rigid film surrounding water droplet looks similar to plastic wrap.

Figure 6 Photomicrograph of water-in-oil emulsion showing two water droplets touching but unable to merge because of film around droplets.

(from API, 1974)

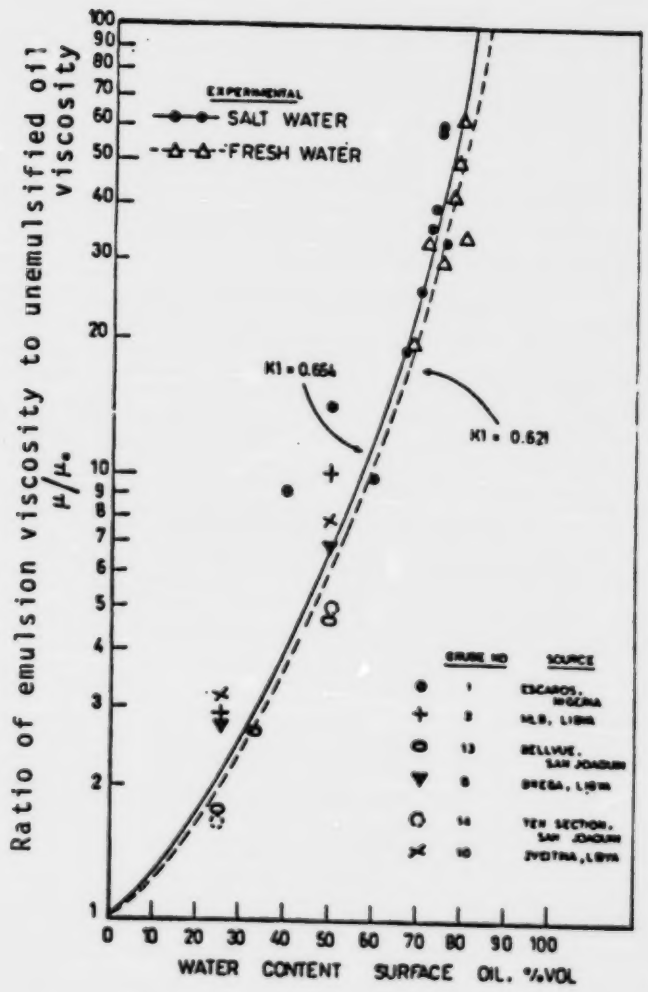
TABLE 1

Consequences of emulsification of oil with time

Oils	After 4 hours			After 24 hours			After 168 hours		
	Volume change %	Water %	Viscosity cP at 20 C	Volume change %	Water %	Viscosity cP at 20 C	Volume change %	Water %	Viscosity cP at 20 C
Ekofisk	- 10	0	6.5	+ 360	85	- (1)	+ 220	86	1,800
Kuwait	0	3	77	+ 100	70	400	+ 230	82	6,100
Arabian Light	+ 360	88	1.600	+ 260	83	2.950	+ 150	78	6.900
Iranian Light	+ 450	82	1.400	+ 350	84	1.770	+ 240	86	9.000
Marine Diesel Oil	+ 515	84	-	+ 537	82	- (1)	+ 580	82	-

(1) Not measurable because of emulsion

(from CONCAWE,1981)



(from Mackay et al,1979)

FIGURE 7 VISCOSITY VERSUS WATER CONTENT OF EMULSION

TABLE 2

RELATIVE EMULSIFYING TENDENCIES OF CRUDE OILS

EXTREMELY STRONG	VERY STRONG	STRONG	INTERMEDIATE	RELATIVELY WEAK
Kuwait	Iranian Heavy	Arabian Lt	Nigerian Lt.	Berri
La Rosa	Iranian Light	Basrah	Skikda	W. Texas Sour
	Arabian Heavy	Zakum	Lagunillas	Saharan Blend
	Arabian Med.	Tia Juana Lt.	Loolaan	Jobo
	Kirkuk	Guanipa	Sirtic	Brent
	Tia Juana Med.	Isthmus	Murban	Ekofisk
	Sag River	Brega		Flotta
		Minas		Jay
		Bachaquero		Mubarek
		San Joaquin		So. Louisiana
		Agip 100		Qatar
		Ardjuna		Forties
		Sassan		
		Hondo Monterey		
		Hondo Mix		
		- - - Sunniland - - - - - -		
		- - - North Slope - - - - -		
		- - - Hondo Sandstone - - -		
		- - - Suez Mix - - - - - -		

(from Exxon, 1983)

Wave action on a thick, freshly discharged oil spill mixes the oil and water together at the surface. Since there is an abundance of oil at the immediate surface, the water becomes the dispersed phase within the oil and takes the form of droplets having a wide drop size distribution. The large drops quickly sink through the oil and coalesce at the oil slick-water interface; the very small water droplets (in the micron size range), having much less weight to overcome viscous resistance, are retained longer within the oil. The cyclical process described earlier for natural dispersion occurs here as well: water is mixed into the oil, the large water globules quickly migrate from the oil, and the smaller drops are retained.

Eventually even the small droplets would separate out of the oil phase were it not for emulsifying agents or emulsifiers naturally present in the crude oil. These substances include asphaltenes, resinous substances, oil soluble organic acids, carbon particles, etc. These emulsifiers usually occur as a film on the surface of the dispersed droplets, and are indirectly responsible for the retention of the small droplets in the oil and for the ultimate stability and high viscosity of the emulsion. Professor D. Mackay at the University of Toronto has developed an interesting theory to explain the chemistry of oil spill emulsions, but this is too complex to discuss here (Mackay and Zagorski 1982). Suffice to say that most crude oils when spilled on agitated water do form highly viscous, stable emulsions. Clearly,this emulsification process is in direct competition with, and is the greatest obstacle to, the dispersion process.

1.2.4 Treating Emulsions

Water-in-oil emulsification is a major problem that must be dealt with in the oil industry whenever crude oil is contacted and mixed with water. This happens most often in its production from oil fields since both oil and water are contained within the pores that make up all reservoirs. Standard chemical

engineering processes have been developed over the years to treat or "break" these emulsions, that is, to separate the oil from the water.

The factors involved in treating water-in-oil emulsions include:

1. breaking the films surrounding the small water droplets (see Figure 5) and coalescing the droplets to produce larger drops, and
2. settling the water drops during or after their coalescence.

Unless the film is broken, the water droplets do not merge together into coalescence--at least in any reasonable length of time. Therefore, heat, chemicals, electricity, mechanical devices, and various combinations of these are normally required to break the film and cause the water droplets to coalesce (Figures 8 and 9 illustrate chemical treatment).

The higher the viscosity of the water-in-oil emulsion, the slower is the settling rate of the water in it. Thus, if the emulsion is at a low temperature, its viscosity is high, and subsequently the separation of water from the oil is slow. Also, the smaller the water droplets in the oil, the longer it takes for them to separate out. In addition, if the difference in specific gravity between the oil and the water in the emulsion is small then their separation is slow. Therefore, all the various treating practices are directed toward increasing the size of the water droplets, increasing the specific gravity difference between water and oil, and decreasing the viscosity of the oil. Treating brings the water settling rate to an acceptable level.

Unfortunately, the various treatment techniques developed for oil field application are inapplicable for breaking oil spill emulsions in-situ (on the ocean surface). All systems are designed to deal with the emulsion once concentrated and contained, and require intimate and substantial mixing of the emulsion with the treating agent (e.g. chemicals, heat, etc.). In view of the

Figure 8 Photomicrograph of single water droplet in treated emulsion. Note that film is breaking.

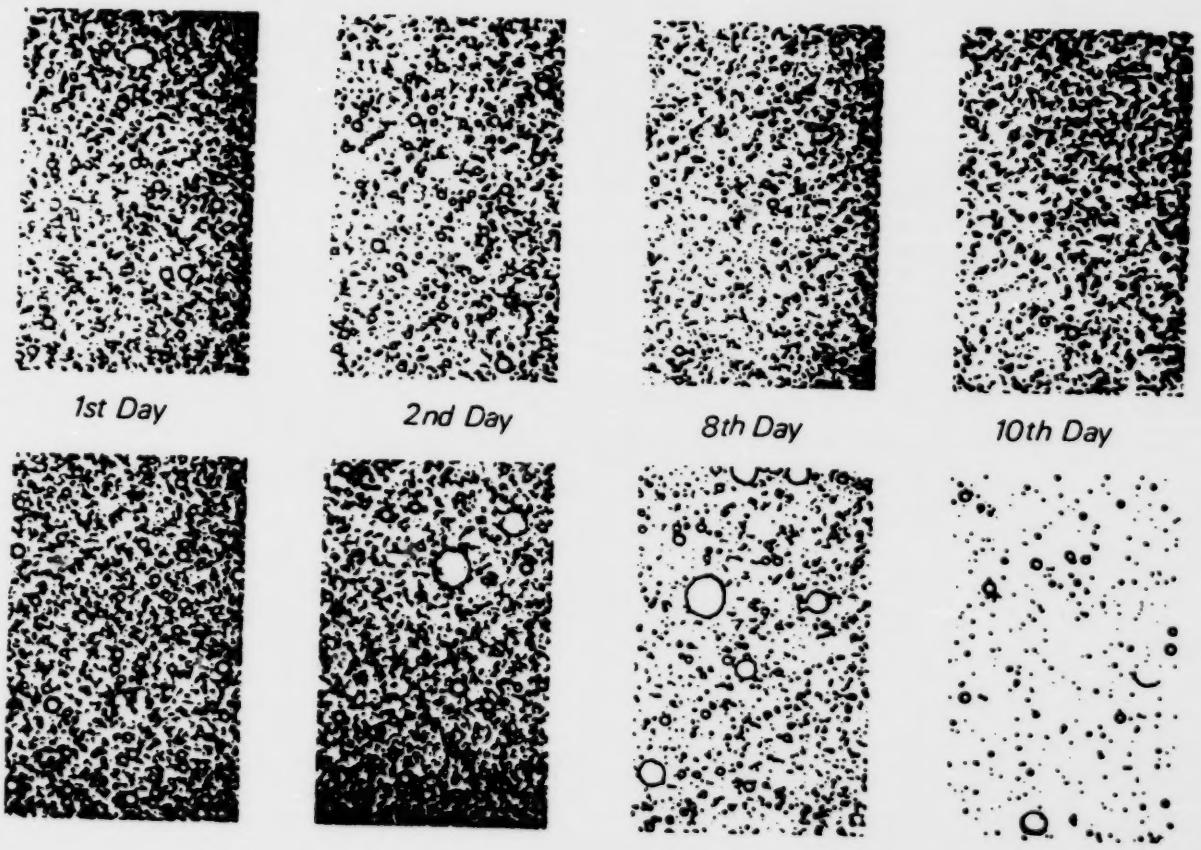


Figure 9 . Two samples of the same water-in-oil emulsion maintained at the same temperature over a number of days. Demulsifier has been added to the lower sample. No chemical has been added to the top sample.

(from API, 1974)

particular stability of oil spill emulsions, their resistance to treatment, and their widely spread nature once formed on the ocean surface, it may not be possible to treat or break emulsions in-situ. Prevention of their formation in the first instance should be a more practical approach to take.

This idea was first investigated by Berridge et al (1968). They mixed low concentrations of an oilfield emulsion breaker (Breaxit) into various fresh crude oils and then tried to emulsify the oils in a blender. The procedure was repeated using a dispersant (BP 1002). The emulsion breaker successfully prevented emulsification while the dispersant was only marginally successful in doing so. Bridie et al (1980), in a study of emulsion breakers for oil spill use, also pre-mixed oils with a Shell product (LA 1834) in concentrations of 300 to 1000 mg/l and then attempted to emulsify them with water. The chemical successfully prevented the formation of stable emulsions. Interestingly, it was noted that it made no difference whether the surfactant was added to the oil or the water. Jones et al (1978), also reported that chemical demulsifiers, when premixed with oil before mixing with water, slow the buildup of the interfacial oil film between water droplets that stabilized emulsions.

1.3 SUMMARY OF PROBLEM

The simultaneous processes of dispersion and emulsification compete to determine whether an offshore oil spill primarily dissipates into the water or remains on the surface as a viscous mass. Evaporation tends to inhibit dispersion but probably enhances emulsification. Which process dominates is probably a function of initial oil properties (oil type, slick thickness, etc.) and environmental conditions (sea state, temperature, etc.). It is usually reasonable to assume that at the initial stages of a spill, dispersion rates are

at their highest, especially for fairly thin slicks. As evaporation continues to increase oil viscosity, emulsification rates undoubtedly exceed dispersion rates and predominate as the primary oil/water mixing process. Although dispersion and emulsification rates vis-a-vis sea state and oil slick properties are not precisely known, any successful attempt to greatly diminish the rate of emulsification (and inhibit enormous increases in viscosity) will likely encourage the ultimate dispersion of the slick. In-situ treatment of the stable emulsion itself once formed must be regarded as impractical. The remaining alternative is to prevent emulsification from occurring at all, or at least inhibiting the process to such an extent that dispersion predominates. The application to the freshly spilled oil of small quantities of a chemical or a combination of chemicals might comprise a practical solution for doing this. This idea was the basis of this study.

1.4 OBJECTIVE OF THE STUDY

The objective of the study was to determine whether certain surfactant chemicals can be practically added to large oil spills at sea to dramatically curtail water-in-oil emulsification and permit dispersion of the oil by natural sea turbulence.

1.5 STUDY APPROACH

The investigation of emulsion inhibition was undertaken in a stepwise manner. The first phase involved a preliminary screening of surfactants and bench-scale testing of parameters that control their performance. This work is covered in Section 2 of this report.

The next phase of the study involved small-scale tank testing of the most promising surfactant to fully investigate the effects of oil type and

environmental parameters on the performance of the chemical in both inhibiting emulsification and promoting dispersion. This work is reported in Section 3.

Standardized dispersant effectiveness testing was also conducted with the chemical to both assess its efficiency as a dispersion promoter and its effect on the action of conventional oil spill dispersants. This work is presented in Section 4.

The final experimental work involved meso-scale tests in a wind-wave tank at more realistic energy levels to confirm the results of the small scale testing and provide more realistic data on the performance of the surfactant for scaling and modelling purposes. This testing is discussed in Section 5.

Section 6 of the report details the results of a mathematical model developed to describe the competitive nature of the dispersion and emulsification processes and the effect of surfactant addition in shifting the equilibrium from emulsion formation to natural dispersion.

The conclusions and recommendations arising from the study are found in Secton 7.

2.0 PRELIMINARY SCREENING AND BENCH SCALE-TESTING OF SURFACTANTS

2.1 PURPOSE

The purpose of this phase of the study was to select for further testing the best emulsion-inhibiting surfactant on the basis of its performance with fresh and weathered crude oils at different temperatures and concentrations.

2.2 METHODS

2.2.1 Test Procedure

The testing of the surfactants involved a modification of the procedures used by Mackay and Zagorski (1982). Aliquots of premixed crude oil and surfactant were prepared with surfactant-to-oil volume ratios of 1:20,000 (about 50 mg/l), 1:10,000 (about 100 mg/l) and 1:5000 (about 200 mg/l) and thoroughly mixed. One hundred ml of water (fresh or 35 ppt saltwater) were added to each of 16 - 250 ml separatory funnels. Ten ml of oil (plain or premixed with various surfactants) were then added to each funnel. Eight of the funnels were then shaken for thirty minutes with a Burrell Wrist-Action Shaker (Plate 1) set at maximum amplitude. These were then removed and allowed to settle while the next eight funnels were shaken.

The height of the oil layer on top of the emulsion and water (Plates 2 and 3) was recorded 5, 10, 20 and 30 minutes after the separatory funnels were removed from the shaker. This procedure was repeated for three cycles after which all separatory funnels were allowed to settle for 18 hours. A final oil layer height was recorded after this. The funnels were cleaned with an alternate rinse of acetone and methylene chloride or toluene. The use of detergents was deliberately avoided. In some tests, after the layers had separated the water was decanted and replaced with clean water to determine whether this affected the surfactant performance.

PLATE 2 An Example of Fully Recovered Oil

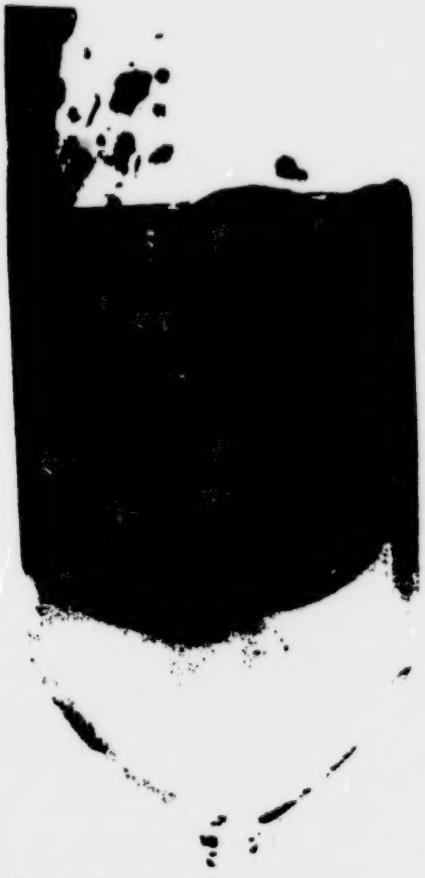


PLATE 3 An Example of a Water-in-Oil Emulsion

PLATE 1 Burrell Wrist-Action Shaker

Tests at 1° and 10°C were conducted in the cold rooms at the River Road Environmental Technology Centre in Ottawa.

2.2.2 Test Oils

Many crude and refined oils were initially screened for their emulsion formation tendencies and stability. The two oils selected for this test program both exhibited a strong tendency to form very stable emulsions, Kuwait crude oil and an Avalon J-34 oil from the Hibernia field. By selecting the most easily emulsifiable and most stable emulsion oils it was felt that the best surfactant for emulsion inhibition could be selected.

Both crude oils were weathered at 15°C in a trough in a wind tunnel to two degrees of evaporative exposure. The evaporative exposure approach to oil weathering (Stiver and Mackay 1983) relates evaporative loss to a dimensionless exposure coefficient containing a mass transfer coefficient, time and oil thickness. This allows lab weathering to be related to oceanic spill conditions. The evaporative loss and properties of each oil is given in Table 3.

TABLE 3

Weathered Oil Characteristics

OIL	EVAPORATIVE EXPOSURE (Θ)	EVAPORATIVE LOSS (wt %)	VISCOSITY (mPas at)		
			0°C	10°C	20°C
J-34	0	0	1,000	198	44
	1.8×10^5	5.6	1,000	324	113
	1×10^6	17.4	1,870	461	125
KUWAIT	0	0	ND		
	2.88×10^5	3.9			
	1.93×10^6	20.8			

* ND = not determined

2.2.3 The Surfactants

Initially six surfactants were screened: two household detergents, one chemical dispersant, two commercial demulsifiers and sodium dioctyl sulfosuccinate (colace). From this screening three chemical mixtures were selected for further performance testing: a 50% by weight mixture of an American manufactured emulsion breaker (Brand X) and toluene; a 50% by weight mixture of a European manufactured emulsion breaker (Brand S) and acetone; and a 50% by weight mixture of colace and propanol. The commercial products were diluted in solvent simply to make dosing of the oil easier.

2.3 RESULTS AND DISCUSSION

Prior to discussing the tabulated results it is useful to point out some of the major observations of the testing.

a) When there was no surfactant included, the J-34 oil and water completely mixed into a brown, stable emulsion at all three test temperatures and stages of weathering. This phenomenon occurred in both fresh and salt water.

b) Surfactant-free, fresh Kuwait oil formed a non-viscous black emulsion at all three temperatures. Weathered Kuwait oil formed brown emulsions only at room temperature. At colder temperatures, the oil appeared to be below its pour point since it formed large viscous lumps suspended in the water (rather than a water-in-oil emulsion) upon shaking.

c) In the cases where the Kuwait oil did not form a true brown emulsion (or "mousse"), an unstable black emulsion formed. This non-viscous black emulsion was typically no more than 4 mm thicker than the initial oil phase height of 7-9 mm, and contained large water droplets.

d) When a surfactant allowed the entire oil phase to separate and rise to the water surface after being agitated, the water phase remained cloudy with very small oil droplets.

e) Brand S was found to be soluble only in the respective oils and not in the water phase and thus was not "rinsed" out of the oil. Brand X and Colace were depleted from the oil when the water phase was decanted from the separatory funnel.

The data accumulated throughout this bench scale testing are summarized in Tables 4 through 9. The six tables contain an evaluation of the individual surfactant performances for every test performed. These evaluations are based upon the average oil phase height recorded (13 in total) during the settling periods. The following provides a short summary of surfactant performance as tabulated.

In tests with J-34 oil, all three surfactants failed in preventing the oil from forming an emulsion at 1°C. Brand X was only effective in salt water at 20°C at a concentration of 5000:1 for all three stages of oil weathering. Colace also appeared to work only in salt water and only with limited success at a concentration of 5000:1. Brand S performed well in both salt and fresh water at 20°C at concentrations of 10000:1 or 5000:1 and to a limited extent at 5000:1 at 10°C.

In tests involving Kuwait oil, each surfactant performed noticeably better. At 20°C Brand X was successful at all three concentrations, at 10°C it worked only at 5000:1 and at 1°C it was completely ineffective. Colace performed well at all the concentrations in fresh Kuwait oil at 20°C. Brand S was effective in fresh Kuwait oil at 20°C, but also performed well in weathered Kuwait oil at concentrations of 10000:1 and 5000:1. At 10°C, Brand S worked to a limited exent at a 10000:1 concentration and fairly well at 5000:1. At 1°C, Brand S operated only to a limited extent at a 5000:1 concentration.

TABLE 4

A SUMMARY OF SURFACTANT PERFORMANCE
J-34 CRUDE OIL AT 20°C

20°C	J-34 CRUDE OIL								
WEATHERING /	BRAND S			BRAND X			COLACE		
WATER TYPE	20000:1	10000:1	5000:1	20000:1	10000:1	5000:1	20000:1	10000:1	5000:1
no/salt	A	A	A	D	D	A	A	A	A
no/fresh	C	A	A	D	D	D	–	–	–
25 hrs/salt	D	A	A	D	D	C	–	–	–
25 hrs/fresh	D	C	A	D	D	D	–	–	–
144 hrs/salt	D	A	A	D	D	A	–	–	–
144 hrs/fresh	D	A	A	D	D	D	–	–	–

LEGEND: A - GOOD (>90% recovery)
B - FAIR (50%<recovery<90%)
C - POOR (10%<recovery<50%)
D - BAD (<10% recovery)

NOTE: ALL SIX TESTS INVOLVING SURFACTANT-FREE OIL HAD LESS THAN 10% RECOVERY

TABLE 5 A SUMMARY OF SURFACTANT PERFORMANCE
KUWAIT OIL AT 20°C

20°C	KUWAIT OIL								
WEATHERING /	BRAND S			BRAND X			COLACE		
WATER TYPE	20000:1	10000:1	5000:1	20000:1	10000:1	5000:1	20000:1	10000:1	5000:1
no/salt	A	A	A	A	A	A	A	A	A
no/fresh	A	A	A	A	A	A	A	A	A
24 hrs/salt	D	A	A	D	D	C	–	–	D
24 hrs/fresh	D	A	A	D	D	D	–	–	D
161 hrs/salt	D	A	A	–	D	D	–	D	D
161 hrs/fresh	D	A	A	–	D	D	–	D	D

LEGEND: A - GOOD (>90% recovery)
B - FAIR (50%<recovery<90%)
C - POOR (10%<recovery<50%)
D - BAD (<10% recovery)

NOTE: ALL SIX TESTS INVOLVING SURFACTANT-FREE OIL HAD LESS THAN 10% RECOVERY

TABLE 6

SUMMARY OF SURFACTANT PERFORMANCE
J-34 CRUDE OIL AT 10°C

10°C	J-34 CRUDE OIL								
WEATHERING /	BRAND S			BRAND X			COLACE		
WATER TYPE	20000:1	10000:1	5000:1	20000:1	10000:1	5000:1	20000:1	10000:1	5000:1
no/salt	D	C	A	D	D	D	D	D	C
no/fresh	D	D	A	D	D	D	D	D	D
25hrs/salt	D	D	A	D	D	D	D	D	D
25hrs/fresh	D	D	B	–	D	D	D	D	D
144hrs/salt	–	D	D	–	–	–	D	D	D
144hrs/fresh	–	D	D	–	–	–	–	–	–

LEGEND: A - GOOD (>90% recovery)
B - FAIR (50%<recovery<90%)
C - POOR (10%<recovery<50%)
D - BAD (<10% recovery)

NOTE: ALL SIX TESTS INVOLVING SURFACTANT-FREE OIL HAD LESS THAN 10% RECOVERY

TABLE 7

SUMMARY OF SURFACTANT PERFORMANCE
KUWAIT OIL AT 10°C

10°C	KUWAIT OIL								
WEATHERING /	BRAND S			BRAND X			COLACE		
WATER TYPE	20000:1	10000:1	5000:1	20000:1	10000:1	5000:1	20000:1	10000:1	5000:1
no/salt	C	A	A	D	D	A	–	–	–
no/fresh	C	A	A	D	C	A	–	–	–
24hrs/salt	E	E	E	E	E	E	–	–	E
24hrs/fresh	E	E	E	E	E	E	–	–	E
161hrs/salt	D	D	B	–	D	D	–	D	D
161hrs/fresh	D	C	B	–	D	D	–	D	D

LEGEND: A - GOOD (>90% recovery)
B - FAIR (50%<recovery<90%)
C - POOR (10%<recovery<50%)
D - BAD (<10% recovery)

NOTE: ALL SIX TESTS INVOLVING SURFACTANT-FREE OIL HAD LESS THAN 10% RECOVERY

TABLE 8

SUMMARY OF SURFACTANT PERFORMANCE
J-34 CRUDE OIL AT 1°C

1°C	J-34 CRUDE OIL								
WEATHERING /	BRAND S			BRAND X			COLACE		
WATER TYPE	20000:1	10000:1	5000:1	20000:1	10000:1	5000:1	20000:1	10000:1	5000:1
no/salt	D	D	C	D	D	D	D	D	C
no/fresh	D	D	D	D	D	D	D	D	D
25 hrs/salt	D	D	D	D	D	D	D	D	C
25 hrs/fresh	D	D	D	D	D	D	D	D	D
144 hrs/salt	–	D	D	–	–	–	D	D	C
144 hrs/fresh	–	D	D	–	–	–	–	–	–

LEGEND: A - GOOD (>90% recovery)
B - FAIR (50%<recovery<90%)
C - POOR (10%<recovery<50%)
D - BAD (<10% recovery)

NOTE: ALL SIX TESTS INVOLVING SURFACTANT-FREE OIL HAD LESS THAN 10% RECOVERY

TABLE 9

SUMMARY OF SURFACTANT PERFORMANCE

KUWAIT OIL AT 1°C

1°C	KUWAIT OIL								
WEATHERING /	BRAND S			BRAND X			COLACE		
WATER TYPE	20000:1	10000:1	5000:1	20000:1	10000:1	5000:1	20000:1	10000:1	5000:1
no/salt	D	D	A	D	D	C	–	–	–
no/fresh	D	C	C	D	D	D	–	–	–
24hrs/salt	E	E	E	E	E	E	–	–	E
24hrs/fresh	E	E	E	E	E	E	–	–	E
161hrs/salt	D	D	D	–	D	D	–	D	D
161hrs/fresh	D	D	D	–	D	D	–	D	D

LEGEND: A - GOOD (>90% recovery)

B - FAIR (50%<recovery<90%)

C - POOR (10%<recovery<50%)

D - BAD (<10% recovery)

E - BAD (i.e. oil formed a semi-solid)

NOTE: ALL SIX TESTS INVOLVING SURFACTANT-FREE OIL HAD LESS THAN 10% RECOVERY

Table 10 provides a relationship between temperature, degree of weathering and surfactant effectiveness for Brand S. It is evident that surfactant effectiveness increases with an increase in temperature or a decrease in viscosity; however, it still is not clear which parameter, temperature or viscosity, has the most influence on surfactant effectiveness.

It should be noted that while the physical results obtained after agitating the oil and water are reproducible, the oil phase height was difficult to measure. In those cases where the emulsion-oil interface was not very well defined, the recorded oil phase height contained an estimated error of 25%. This error was reduced to about 10% as the interface became more defined over the course of the settling period. There was also a 5% error in the surfactant concentrations which was due to the accuracy of the measuring instruments.

Brand S was found to be effective even after decanting the water and replacing it several times; Brand X and Colace were not as effective when the water phase was replaced. Environmental properties of the surfactants may be found in Table 11. Vapour pressures were estimated using gas chromatography, interfacial tensions were determined using a du Nuoy ring and oil-water partition coefficients were estimated using high-pressure liquid chromatography and partitioning experiments. These analyses indicated that all the surfactants have extremely low vapour pressures and thus are unlikely to evaporate significantly. Brand "S" and Colace have far lower vapour pressures than Brand "X". Brand "S" has the lowest oil-water partition coefficient by an order of magnitude. All three surfactants reduce oil-water interfacial tensions significantly even at very low concentrations (1:10,000). Of the three, Brand "S" has the most consistent effect.

TABLE 10

QUANTITATIVE PERFORMANCE OF BRAND "S" IN SALT WATER

TEMPERATURE (°C)	OIL TYPE	EVAPORATIVE LOSS MASS (%)	% OIL RECOVERY AT INDICATED SURFACTANT CONCENTRATION			
			1:20,000	1:10,000	1:5,000	NONE
20	J-34	0	89	76	80	7
		5.6	7	91	86	7
		17.4	9	90	90	7
	KUWAIT	0	93	93	93*	7+
		3.9	7	93	93	7
		20.8	7	93	93	7
10	J-34	0	7	14	93	7
		5.6	7	7	93	7
		17.4		7	7	7
	KUWAIT	0	37	93	93	7
		3.9	7	7	7	7
		20.8	7	7	40	7
1	J-34	0	7	7	24	7
		5.6	7	7	7	7
		17.4	7	7	7	7
	KUWAIT	0	7	15	64	7
		5.6	7	7	7	7
		17.4	7	7	7	7

\+ represents oil dispersed and stuck to glassware
* maximum possible recovery

TABLE 11

PROPERTIES OF SURFACTANTS

	Vapour Pressure @ 20°C (Pa)	Oil-Water partition Coefficient (K_{ow})	Oil-Water Interfacial Tension at 1:10,000 (mN/m)	
			Kuwait	J-34
BRAND "X"	0.3	10^3	0.8	30.7
COLACE	0	10^3	3.3	10.4
BRAND "S"	5×10^{-6}	10^4	2.2	2.6

2.4 SUMMARY AND CONCLUSIONS

a) A 20000:1 oil-to-inhibitor ratio appears to be the lower limit of surfactant performance since all three surfactants had success only with fresh oil at this concentration.

b) Water salinity appears to be a factor in the performance of the surfactants tested. Although Brand S was not affected by salinity, both Brand X and Colace performed noticeably better in salt water tests involving the J-34 oil.

c) Although Table 10 indicates that surfactant performance increases with increased temperature and decreased viscosity, it is not clear whether both parameters contribute to this better performance, or whether only one parameter is responsible.

d) Although Kuwait oil has a reputation for easily forming a stable emulsion, this was not the case in the bench scale testing.

e) Brand S was the best surfactant tested. It was shown to be effective over a wide range of conditions and to have potential for working for long periods because of its oleophilic properties.

3.0 SMALL-SCALE EFFECTIVENESS TESTING

3.1 PURPOSE

The purpose of this phase of the study was to evaluate the performance of the Brand S surfactant in inhibiting emulsification in a larger scale test apparatus over longer time periods than the shaker system. In addition the purpose was to assess the effect of the chemical on the competitive nature of emulsification and dispersion. Oil type, weathering, surfactant concentration, temperature, mixing energy, slick thickness and method of surfactant application were parameters to be varied during the experimental work.

3.2 METHODS

3.2.1 Apparatus

This testing was conducted in a 42x42x42 cm tank filled to a depth of 20 cm with 34 L of water (Plate 4) and fitted with a variable-speed, vertically oscillating hoop to generate radial waves. The tank contained a 42 cm diameter circular plexiglass insert that served to reflect the waves and thus hold the test oil in the centre of the tank to minimize edge effects.

Grab samples of emulsion were taken periodically and analysed for water content by a spectrophotometric technique. Dispersed oil concentrations were analysed similarly.

3.2.2 Test Matrix

The test programme included the following variables:

* two water salinities (fresh and 35 ppt)
* three temperatures (0°C, 10°C, and 20°C)
* three states of weathering (fresh crude, 1 and 5 days exposure)
* oil slick thickness (1.5 mm and 5 mm)

PLATE 4 - HOOP TANK APPARATUS

* two levels of mixing energy of the hoop apparatus (150 rpm and 220 rpm)
* two crude oils: Alberta Sweet Mixed Blend (substituted for Kuwait) and Avalon J-34 crude oil (see Tables 12 and 13)
* four surfactant-to-oil ratios: (0:10,000, 1:5000, 1:1000)
* and three methods of chemical application: pre-mixed, dropwise and sprayed on.

Brand S, a commercial demulsifier which is manufactured in Europe was the surfactant used in these tests. It is non-ionic in nature, has a pour point below -10°C, a water solubility of less than 0.01% and a density of 1.02 g/ml at 20°C. Because it is highly viscous (dynamic viscosity of 1170 cP at 20°C) it was necessary to dilute the product 50% by volume with acetone in order to facilitate the use of a microlitre syringe to deliver the small volumes required in the tests.

3.2.3 Experimental Procedure

Each test was conducted as follows:

1. Prepare approximately 34 L of 35 ppt (parts per thousand) salt water in the 77 L glass tank.
2. Position the vertically oscillating hoop mechanism over the tank and set the hoop oscillating at 150 or 220 rpm.
3.* Use a microlitre syringe to add the surfactant to a 150 mL quantity of crude oil on a volume-to-volume basis and mix vigorously.
4. Pour the 150 mL pre-mixed oil into the centre of the 30.5 cm I.D. oscillating hoop.

---

* NOTE: In the case of dropwise or sprayed on surfactant application ignore step 3 and continue with step 4 by pouring 150 mL of plain oil into the tank which is immediately followed by a dropwise addition of the surfactant using a microlitre syringe or a sprayed on application using a fine mist spray bottle.

TABLE 12:

Physical Properties of the Alberta Sweet Mix Blend Crude Oil

Mass Evaporated (%)	0			20.5			26.7		
Evaporative Exposure (Θ)	0			5.1×10^4			2.5×10^5		
Temperature (^oC)	20	10	0	20	10	0	20	10	0
Oil Density (g/cm^3)	0.8415	0.8760	0.8885	0.8421	0.8857	0.8977	0.8455	0.8885	0.9010
Oil/Water Interfacial Tension (mN/m)	26.5	26.4	27.0	24.4	*	*	25.0	*	*
Oil Viscosity (mPas)	4.8	7.8	15.3	68.4	312	376400	328	147200	446000
Oil Pour Point (^oC)		-4			19			22	

* Oil was too viscous for interfacial tension measurements.

TABLE 13:

Physical Properties of the Avalon J-34 Crude Oil

Mass Evaporated (%)	0			10.4			11.9		
Evaporative Exposure ( )	0			8.1×10^4			3.6×10^5		
Temperature (^oC)	20	10	0	20	10	0	20	10	0
Oil Density (g/cm^3)	0.8753	0.8885	0.8893	0.8974	0.9081	0.9102	0.9054	0.9156	0.9181
Oil/Water Interfacial Tension (mN/m)	28.7	34.5	*	31.8	*	*	31.2	*	*
Oil Viscosity (mPas)	39.6	173	268400	228	87200	480000	640	108000	1026000
Oil Pour Point (^oC)		21			24			25	

* Oil was too viscous for interfacial tension measurements.

5. Draw off approximately 80 mL of water from the sampling port centrally located at the bottom of the tank, 19 cm below the surface of the water.
6. Add the 80 mL dispersion sample along with 25 mL of toluene to a 250 mL separatory funnel, shake well and let sit for 30 minutes.
7. Collect approximately 1 g of emulsion.
8. Immediately after taking an emulsion sample weigh out 1.0 g and add it, along with 25 mL of toluene, to a separatory funnel, shake well and let sit for 30 minutes.
9. Repeat steps 5 to 8 at 0, 0.25, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 hours.
10. Decant and record the water volume in the separatory funnel of the dispersion sample.
11. Decant and record the volume of the remaining oil/toluene phase.
12. Using a spectrophotometer and a known standard, determine the oil content in the oil/toluene phase in parts per million.
13. Repeat steps 10 to 12 for each dispersion sample.
14. Decant and discard the water in the emulsion sample separatory funnel.
15. Decant and record the volume of the remaining oil/toluene phase.
16. Using a spectrophotometer and a known standard, determine the oil content in the oil/toluene phase in grams of oil per litre of toluene.
17. Repeat steps 14 to 16 for each emulsion sample.
18. Clean the glassware with an alternate rinse of toluene and acetone.
19. Remove and wipe clean the oscillating hoop.
20. Drain and wipe the glass tank. Then, using warm water at high pressure, rinse off the tank.

3.3 RESULTS AND DISCUSSION

The agitation of the surfactant/oil/water mixtures typically resulted in one of four possibilities depending on the experimental conditions. One was the formation of a viscous brown emulsion or "mousse", evident as a circular patch about 2 cm thick and 17 cm in diameter that floated at the water surface and resulted in little or no dispersion.

A second possibility was the total dispersion of the oil slick in the form of droplets with diameters much less than 1 mm. This made the water phase extremely cloudy and dark brown in colour or even black and opaque.

Third, was the formation of a weak, black coloured emulsion having large (1 mm diameter) water droplets mixed throughout. These emulsions had viscosities only marginally greater than their parent oils, contained 20-70% by mass water and resulted in low dispersion concentrations.

Lastly, was the formation of non-coalesing "emulsion" globules which consisted of either pure oil (in those cases where the oil was below its pour point), a weak emulsion (20-70% by mass water content) or a viscous emulsion (75% by mass water or more). These ranged in size from 1-cm diameter globules to thick mats about 10 cm^2 in area.

3.3.1 Emulsification and Dispersion of Fresh Oil

Figure 10 shows the emulsion water content as a function of time for the Avalon J-34 oil (fresh). With no inhibitor present the oil rapidly takes up water, initially in the form of large (about 2 mm) droplets, to form a black lumpy emulsion. These large droplets appear to break down to smaller size ($<$1 mm) over a period of about an hour. After two hours the emulsion turns into the familiar, smooth, brown "mousse" surrounded by a thin ring of the black emulsion. The underside of the emulsion slick is distinctly hilly.

Addition of increasing concentrations of the Brand S inhibitor increasingly delays the onset of emulsion formation. As can be seen on Figure 10 an inhibitor concentration of 1:10,000 delays the onset of emulsification for 1 to 1.5 hours while the addition of 1 part inhibitor in 5,000 parts oil prevents the formation of the emulsion for the entire test period.

FIGURE 10: EMULSIFICATION VS TIME (FRESH J-34 AT 20°C)

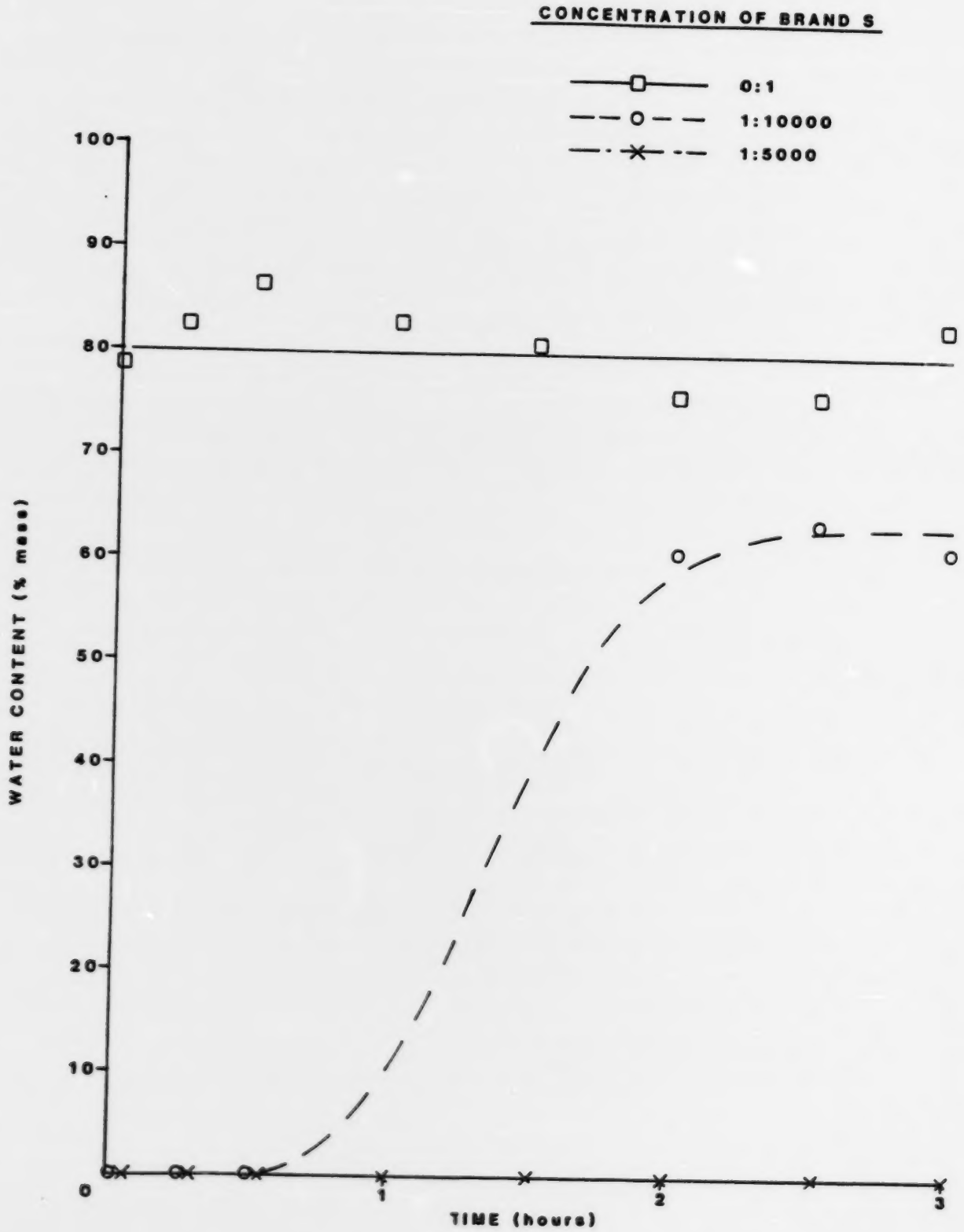


Figure 11 shows the dispersed oil concentrations, measured at the bottom of the tank (about 20 cm below the surface), for each of the three tests with the East Coast oil. It is evident that increasing concentrations of the inhibitor dramatically increase dispersed oil concentrations. Of equal interest is the effect of emulsification on dispersion. Comparing the curves of Figures 10 and 11 for the untreated oil indicates that as the emulsion ages and becomes more viscous (i.e., the water droplets get progressively smaller) the amount of dispersed oil decreases. This implies that the rate of dispersion is decreasing (assuming a constant rate of dispersed oil recoalescence). Over the 3 hour test the dispersed oil concentrations dropped from 150 ppm to about 50 ppm. The visible oil droplets were in the 1 to 5 mm size range. It should be noted that a homogeneously mixed oil concentration of about 4000 ppm would represent all the oil dispersed into the tank.

The competitive nature of emulsification and dispersion is more dramatically demonstrated in comparing the results, on Figures 10 and 11, for the test with 1 part inhibitor in 10,000 parts oil. Initially (prior to emulsification) dispersed oil concentrations rose rapidly to the 900 ppm level but, after about an hour began to fall; after the three hour test when the viscous brown "mousse" has formed, the oil concentration had dropped to 150 ppm. Dispersed oil droplet sizes for the dosed oils were much less than 1 mm in size.

Figure 12 shows similar results for tests run with the Alberta Sweet Mixed Blend (ASMB) crude oil. Addition of 1 part inhibitor to 10,000 parts oil results in the prevention of emulsification over the three hour test. In this case almost all of the oil was immediately dispersed as fine ($\ll$1 mm) droplets yielding a measured concentration of 2000 ppm).

Figure 13 shows that the dispersion concentration for the inhibitor-free oil peaked at about 700 ppm. The droplet sizes were somewhat less than 1 mm. The dispersed oil concentration decreased to 250 ppm after 3 hours, as the oil emulsified. The higher oil-in-water concentrations and smaller droplet sizes for the ASMB crude as compared with the J-34 crude can be attributed to the ASMB crude's lower viscosity and interfacial tension.

FIGURE 11: DISPERSION VS TIME (FRESH J-34)

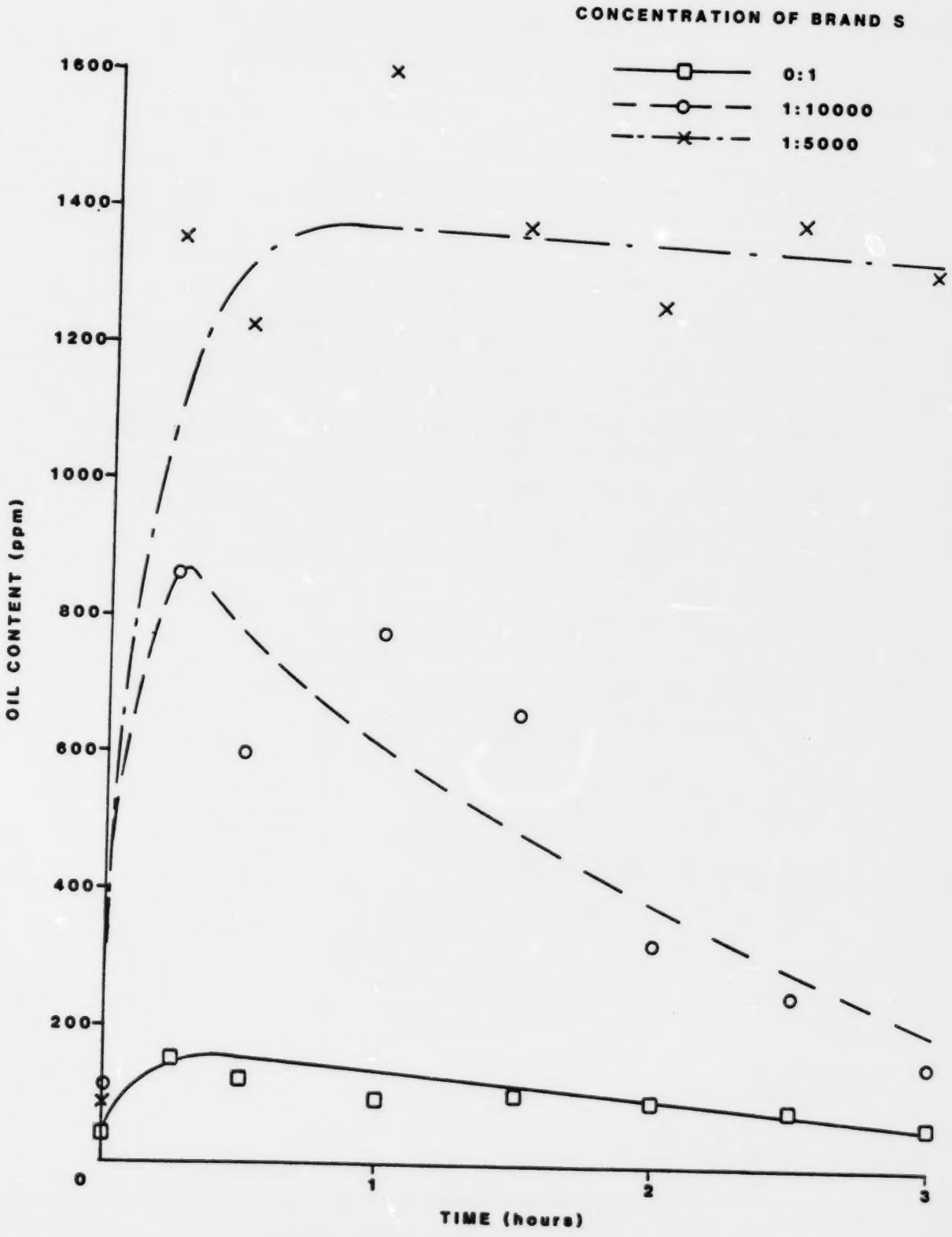


FIGURE 12: EMULSIFICATION VS TIME (FRESH ASMB AT 20°C)

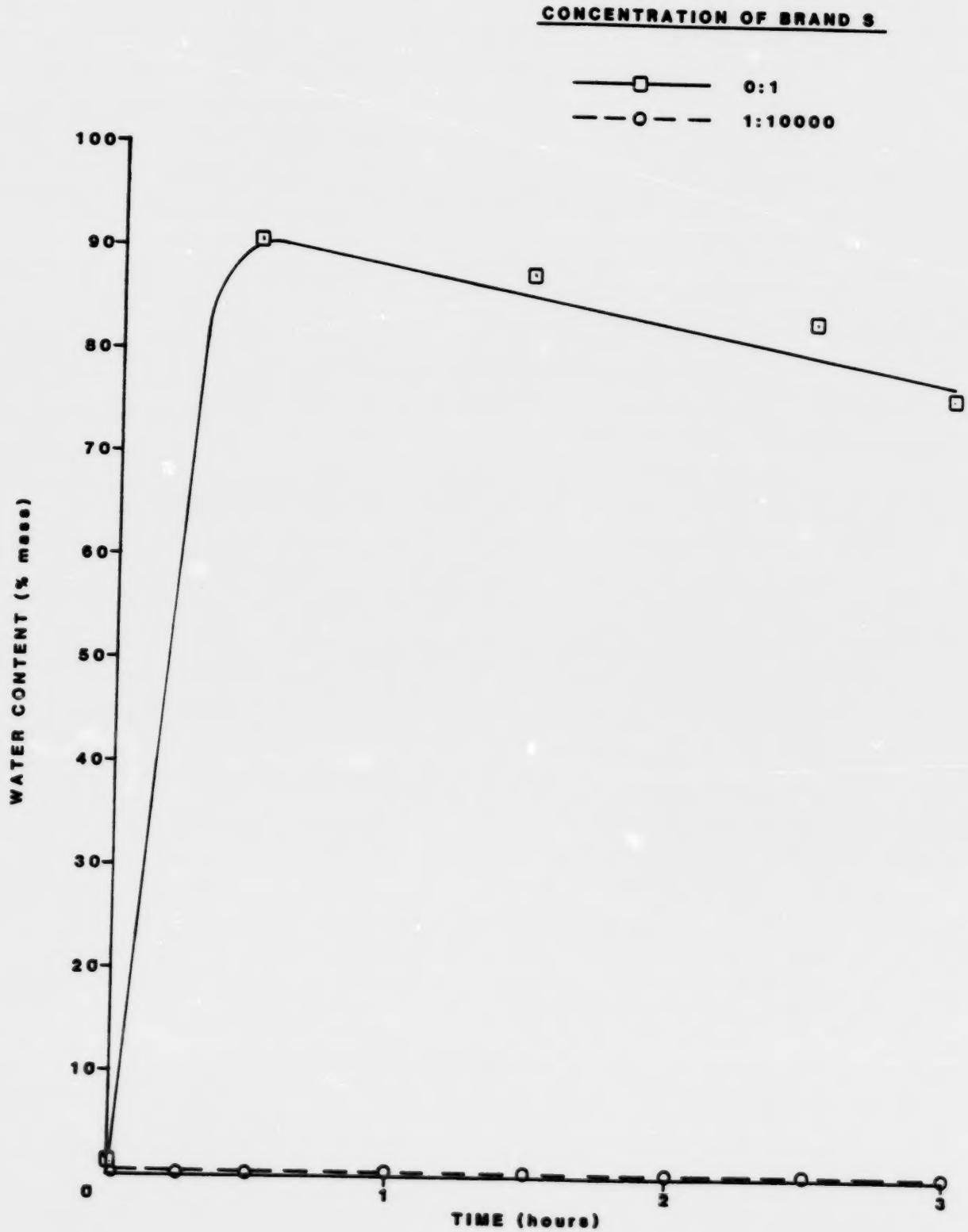
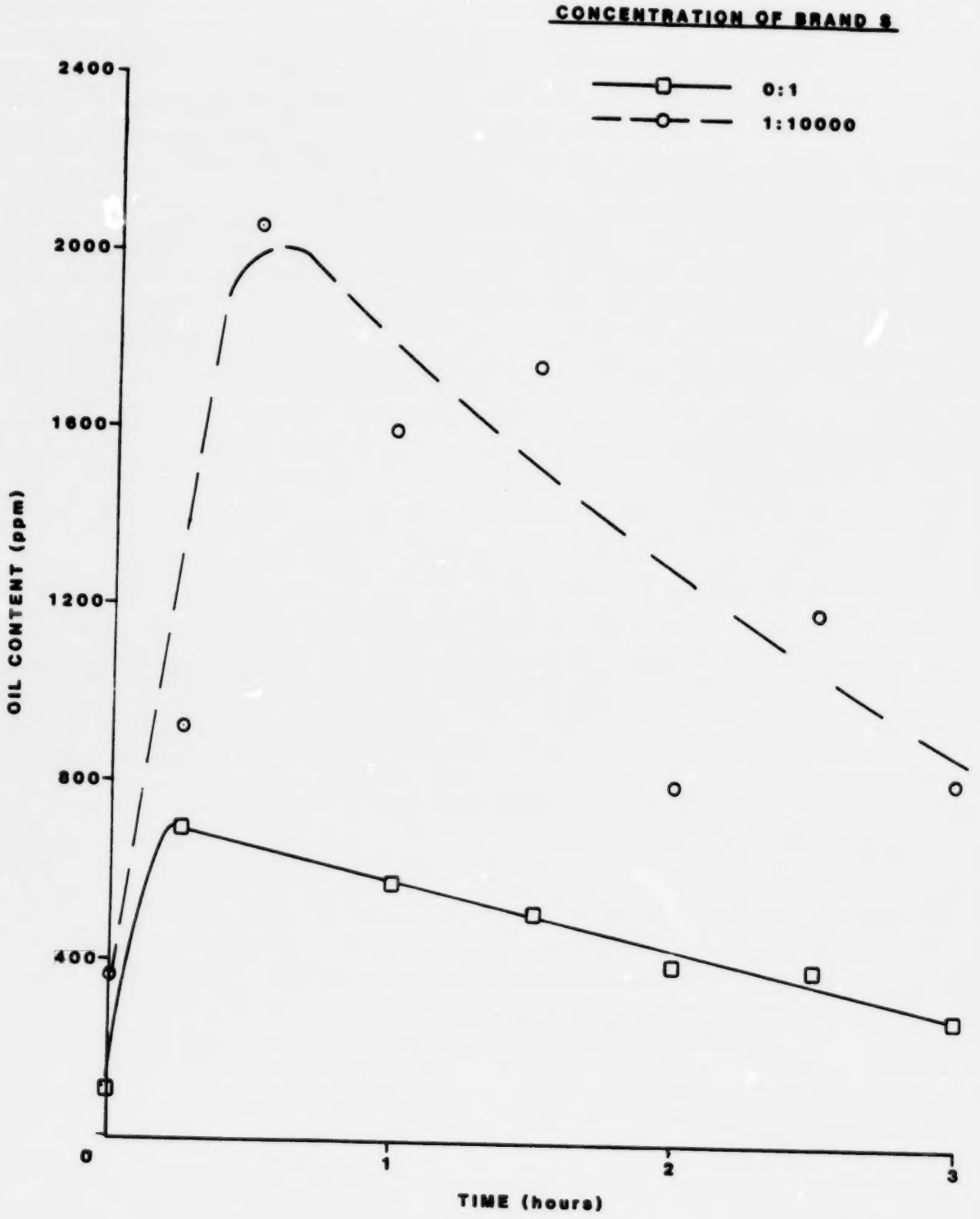


FIGURE 13 : DISPERSION VS TIME (FRESH ASMB)



3.3.2 Effects of Oil Weathering on Surfactant Performance

Figure 14 shows that the emulsion inhibiting performance of the surfactant is affected by oil weathering. With fresh J-34 oil a surfactant-to-oil ratio of 1:10,000 inhibits emulsification for an hour. With the same oil artificially weathered to an evaporative exposure of 8×10^4 (24 hours) a dosage of 1:5000 is required to inhibit emulsification over the entire test period. The same oil weathered to an evaporative exposure of 3.6×10^5 (121 hours) requires a dosage of 1:1000 to inhibit emulsification. It is likely that this effect is related to an increase in bulk oil viscosity, rather than an increase in the relative concentration of natural emulsion-stabilizing compounds in the weathered oil. The dose of surfactant required to inhibit emulsification increases by an order of magnitude over the range of weathering, as does the oil viscosity, while the relative concentration of non-volatile components increases only slightly due to the 12% mass loss to evaporation.

Figure 15 shows the effects of oil weathering on the dispersed oil concentration beneath the dosed slick. As the slick becomes more weathered higher concentations of surfactant are required to achieve the same dispersion. The relationship is different than for emulsion inhibition: dosages of 1:10,000 for fresh and 24 hour weathered and 1:5000 for 121 hour weathered oil achieve similar dispersions. This indicates that factors other than just oil viscosity play a role in determining the dispersion rate enhancement effect of the surfactant. Reduced interfacial tension is known to greatly enhance dispersion.

Figure 16 shows the effects of weathering on the performance of the surfactant in inhibiting emulsification with Alberta Sweet Mixed Blend crude oil. Effective dose rates were 1:10,000 for fresh and 24 hour weathered ($\theta = 5 \times 10^4$) and 1:5000 for 121 hour weathered ($\theta = 2.6 \times 10^5$). The 1:5000 dose for the 121 hour weathered crude initially seemed to be insufficient and a black emulsion began to form, however after 1.5 hours this had completely

FIGURE 14 : EFFECT OF WEATHERING ON SURFACTANT PERFORMANCE
EMULSIFICATION VS TIME (J-34 AT 20°C)

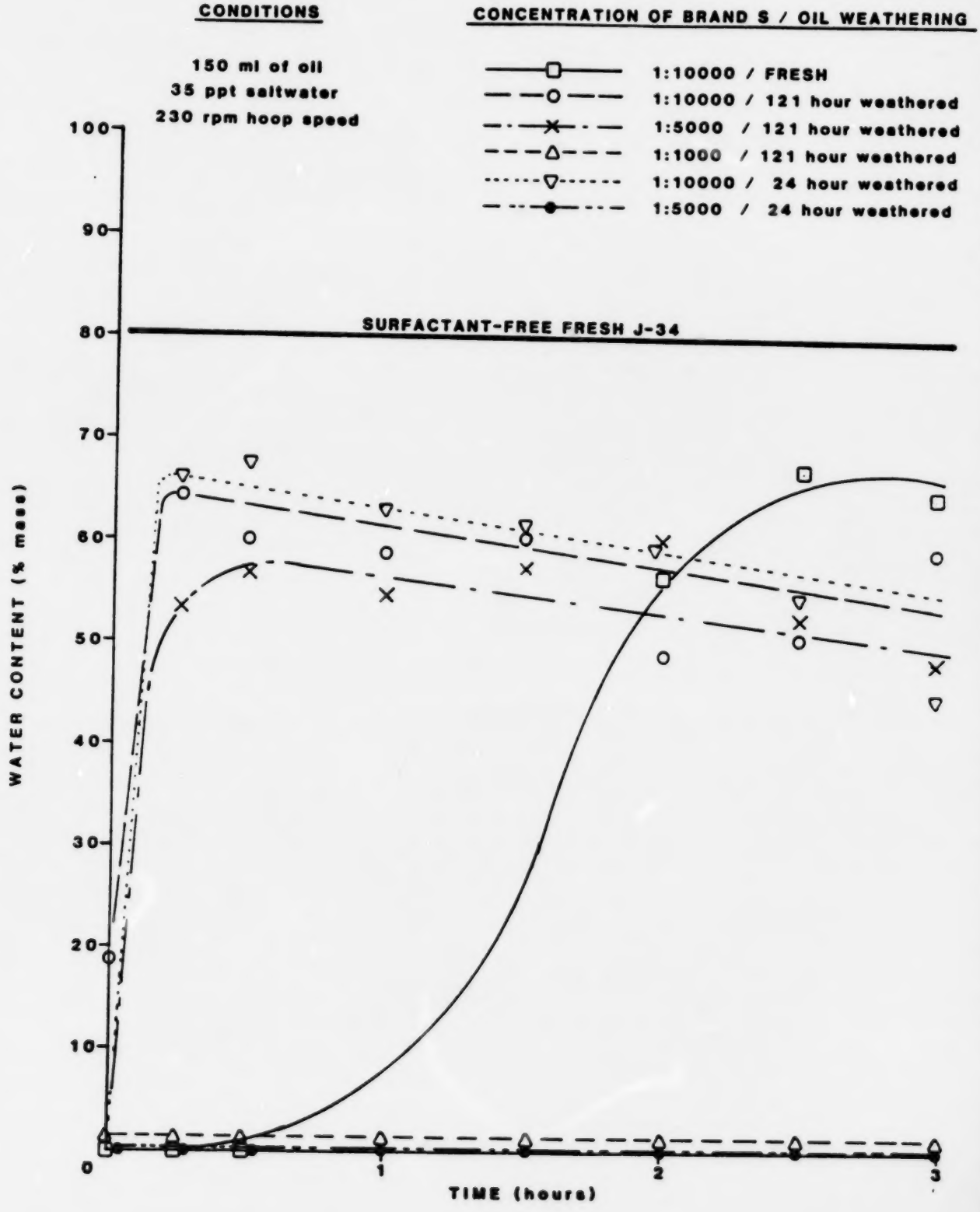


FIGURE 15: EFFECT OF WEATHERING ON SURFACTANT PERFORMANCE
DISPERSION VS TIME (J-34 AT 20°C)

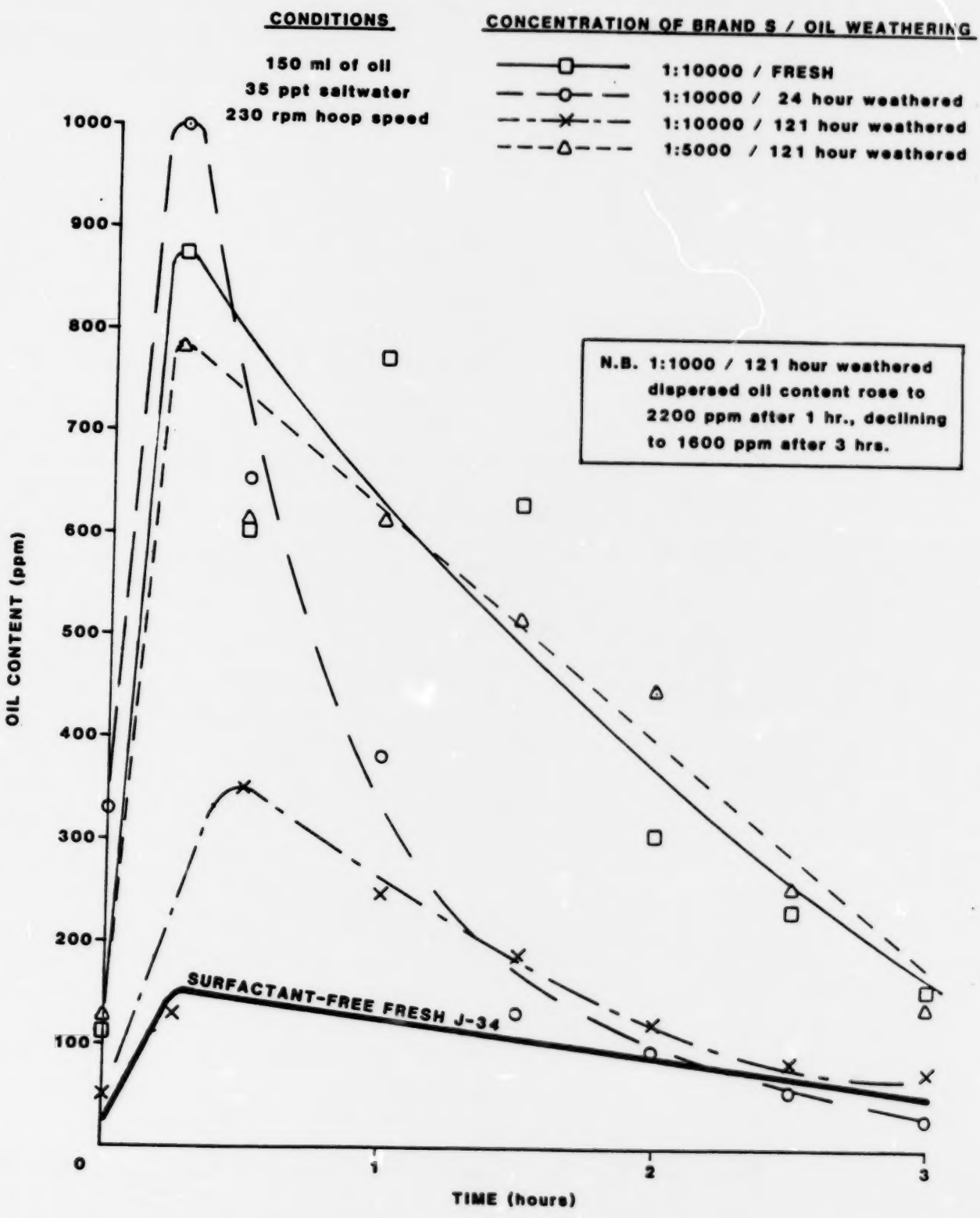
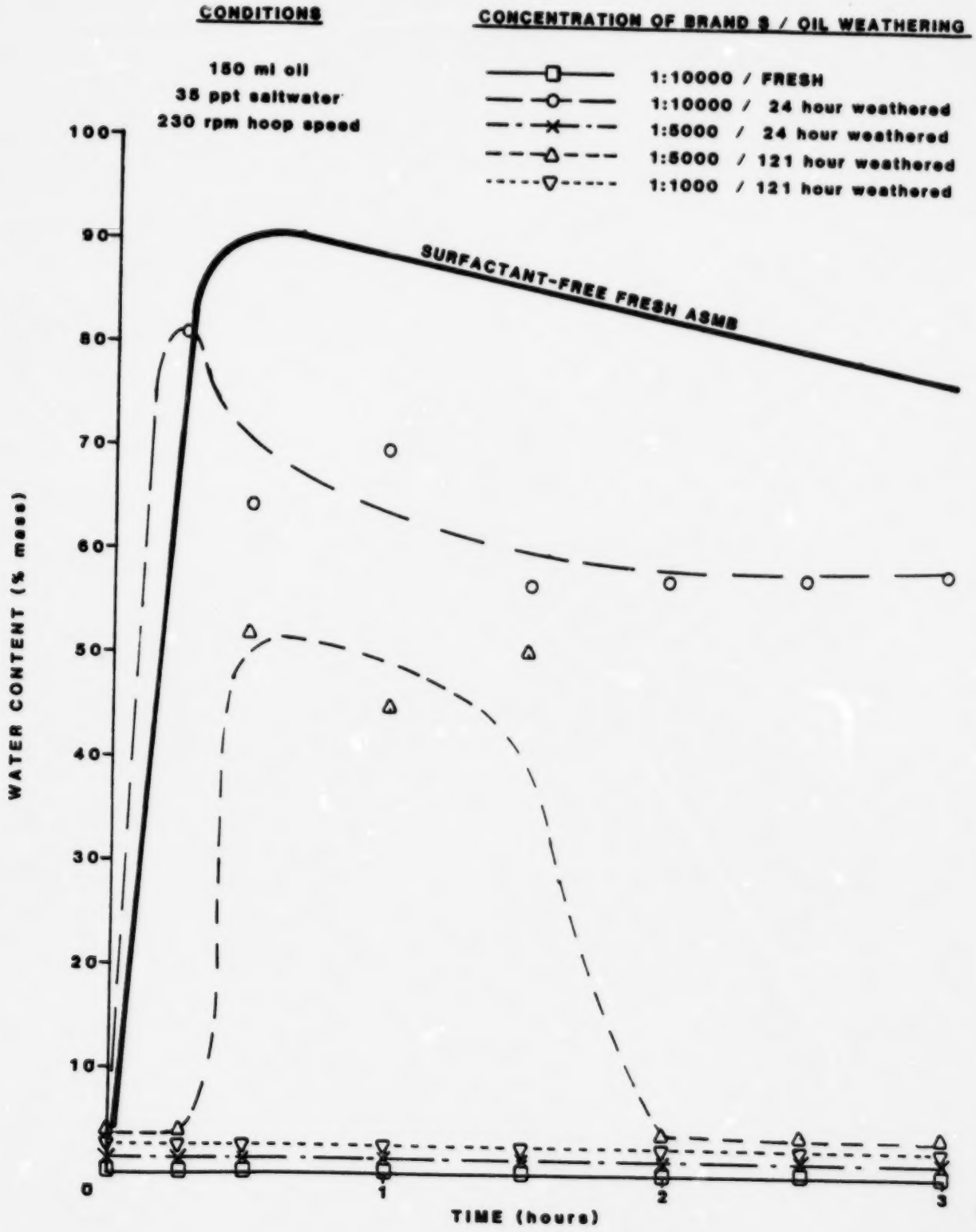


FIGURE 16: EFFECT OF WEATHERING ON SURFACTANT PERFORMANCE
EMULSIFICATION VS TIME (ASMB AT 20 °C)



dispersed. As with the J-34 oil, the oil viscosity seems to be the dominating factor in controlling surfactant performance. In fact, the 121 hour weathered ASMB (with a viscosity of 330 mPas at 20°C) required the same dose rate as 24 hour weathered J-34 (230 mPas at 20°C) to inhibit emulsification.

Figure 17 shows the dispersed oil concentrations for the runs shown on Figure 16. Since a concentration of about 4,000 ppm represents all the oil homogenously mixed in the 34 L tank, it is clear that the surfactant, in the case of ASMB, shifts the equilibrium from emulsification to complete dispersion for doses of 1:5000 for 24 hour and 1:1000 for 121 hour weathered crude oil. Lower concentrations (above the minimum required) inhibit emulsification without resulting in complete dispersion (e.g., 1:10,000 in fresh oil).

3.3.3 Effects of Temperature on Surfactant Performance

Figure 18 shows the effect of temperature on the performance of surfactant in inhibiting emulsification for fresh and weathered J-34 oil. As the temperature decreases, higher concentrations of surfactant are required to prevent emulsification. For example, fresh J-34 requires 1:10,000 at 20°C, and 1:5000 at 10°C. Similarly for 24 hour weathered J-34, 1:5000 is required at 20°C and 1:1000 at 10°C. At 20°C 1:1000 easily prevents emulsification of the 121 hour aged oil while at 10°C 1:1000 barely inhibits emulsion formation. Neither weathered oil formed a tightly bound emulsion at 10°C.

It should be noted that the results of Figure 18 appear to show that the chemical was effective with J-34 oil at 0°C in that no emulsion was formed. The fact is that at this temperature, which is about 20°C below the oil's pour point, the oil formed immediately into 1-4 cm diameter balls and remained so throughout the test period.

FIGURE 17: EFFECT OF WEATHERING ON SURFACTANT PERFORMANCE
DISPERSION VS TIME (ASMB AT 20°C)

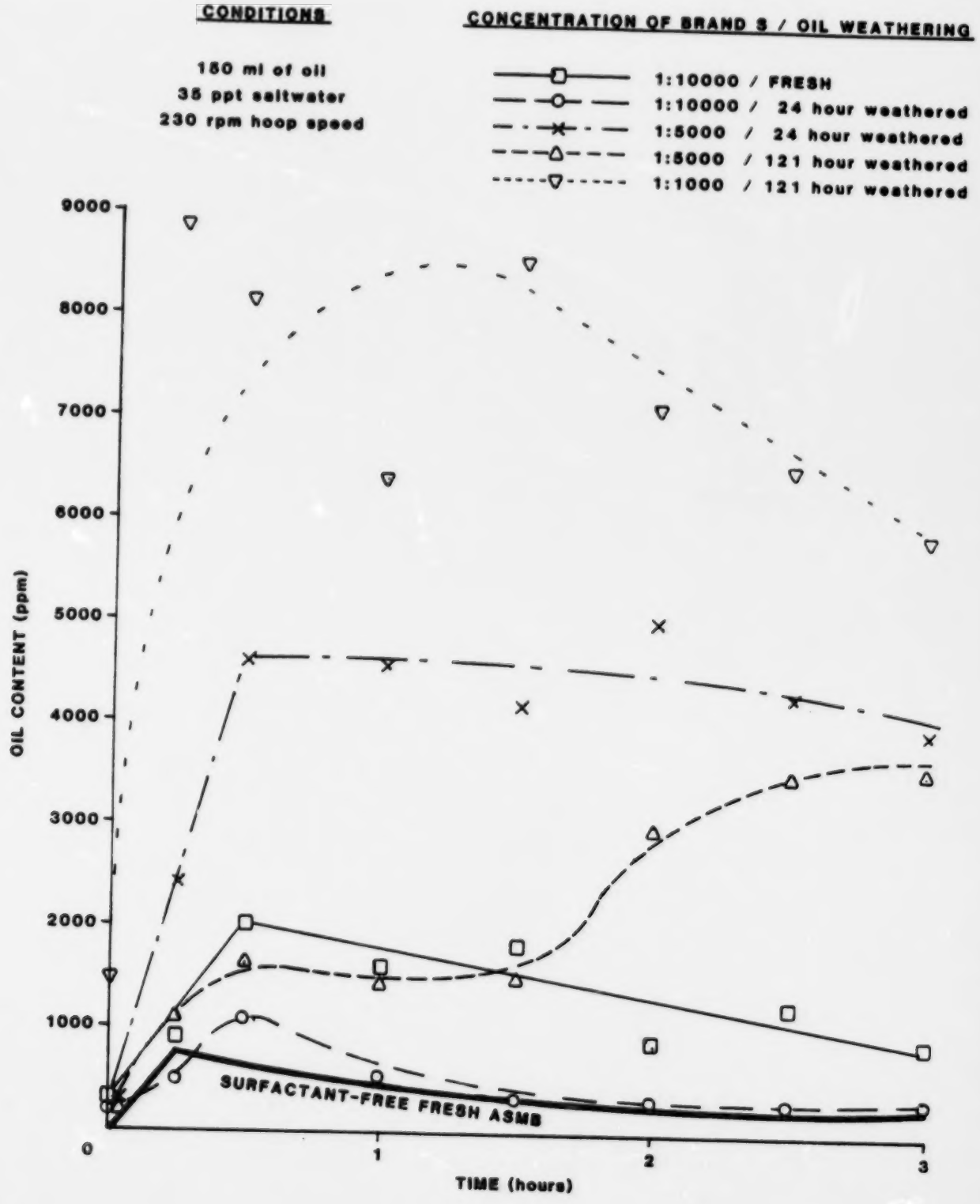
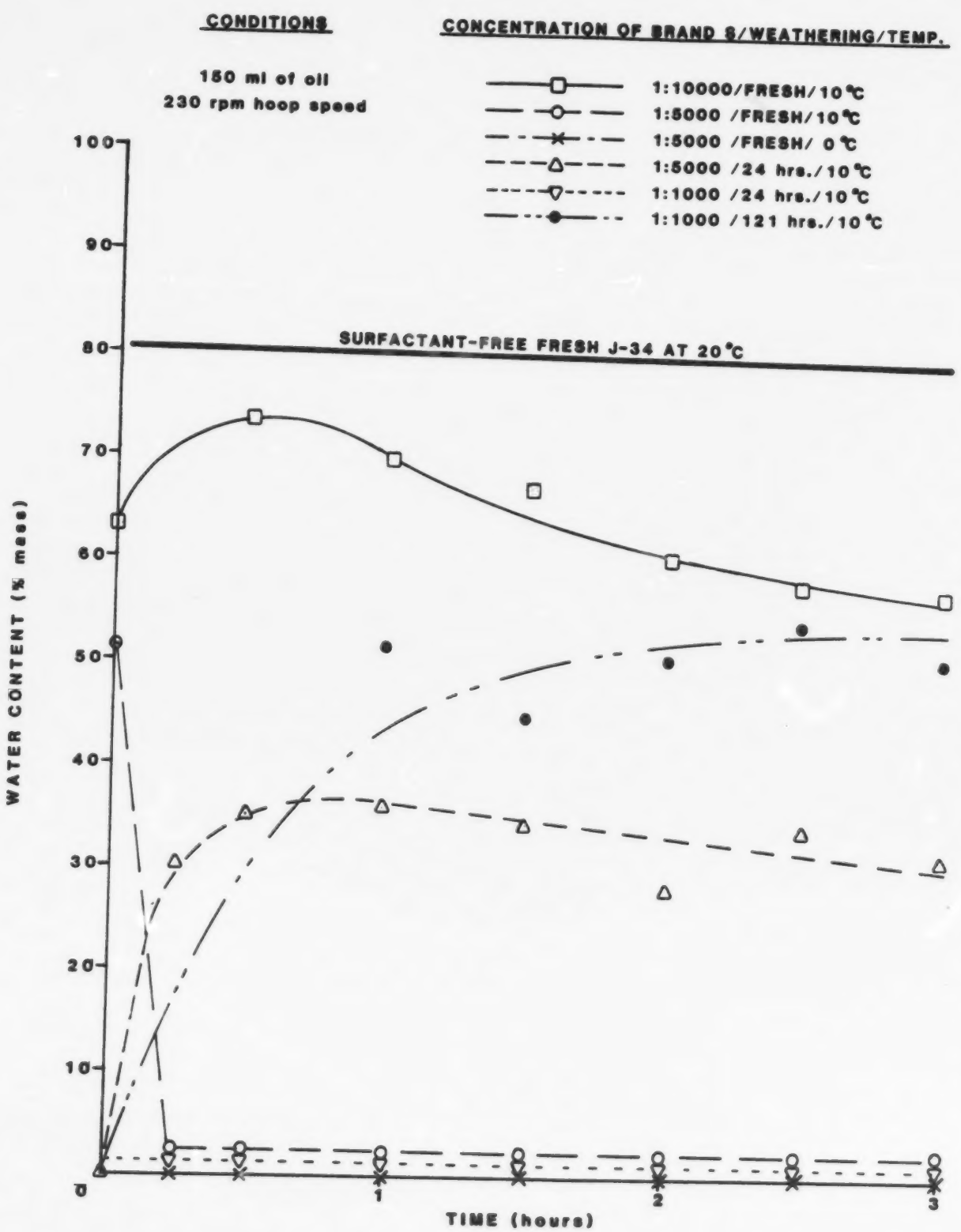


FIGURE 18: EFFECT OF TEMPERATURE ON SURFACTANT PERFORMANCE
EMULSIFICATION VS TIME (J-34)



The above results confirm that oil viscosity plays a key role in determining surfactant performance; for the fresh oil case a drop in temperature from 20° to 10°C results in a fourfold increase in viscosity and a doubling of the surfactant dose is required to prevent emulsification.

As noted, pour point also plays a significant role in emulsification. Once the temperature drops 10 to 15°C below the pour point the oil "gels" even at the relatively high shear rates in the hoop tank. This greatly inhibits the incorporation of water droplets into the oil and the break down of large drops into small drops. As the temperature drops 20°C below the pour point the oil no longer forms a slick or coherent mass; it is fragmented into solid-like balls which do not coalesce, disperse into small droplets or incorporate water.

Figure 19 shows the effect of temperature on dispersed oil concentrations beneath dosed, fresh and weathered J-34 oil. In comparison with Figure 15 a drop in temperature from 20°C to 10°C approximately halves the dispersed oil concentration.

Table 14 presents the results obtained for similar runs with the ASMB crude oil. In this case, because ASMB is less viscous than J-34, the surfactant was more effective with the weathered oils at 10°C. In the case of the 121-hour weathered oil at 10°C, the temperature was far enough below the pour point (22°C) that the oil was beginning to exhibit "gel"-like behaviour.

Dispersed oil concentrations were considerably higher for the ASMB than for the J-34 oil; again because of the ASMB oil's lower viscosity and interfacial tension. A concentration greater than 4000 ppm indicates complete dispersion of the oil sample.

3.3.4 Combined Effect of Weathering and Temperature

Table 15 summarizes the minimum surfactant dosage required to prevent emulsification for both oils as a function of temperature and weathering for the previously discussed tests.

FIGURE 19: EFFECT OF TEMPERATURE ON SURFACTANT PERFORMANCE
DISPERSION VS TIME (J-34)

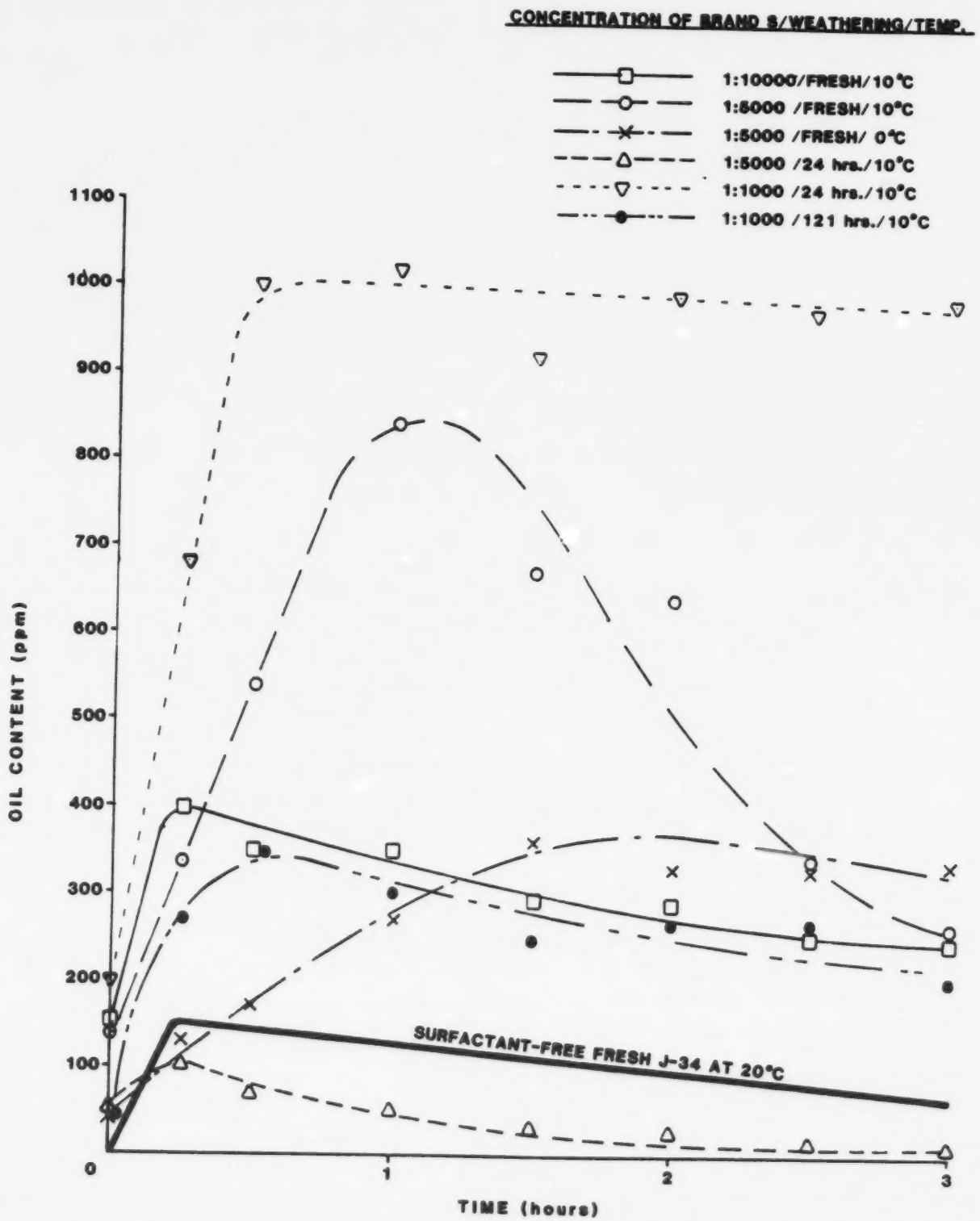


TABLE 14

Effects of Temperature on Surfactant Performance: ASMB

Temperature (°C)	Evaporative Exposure (θ)	Dose of Surfactant (vol:vol)	Final Water Content (% mass)	Final Dispersed Oil Concentration (ppm)
20	0	0:1	80	90
	0	1:10,000	0	800
	5×10^4	1:10,000	60	140
	5×10^4	1:5000	0	4200*
	2.6×10^5	1:5000	0	3500
	2.6×10^5	1:1000	0	6000*
10	0	1:5000	0	5000*
	5×10^4	1:1000	0	2500
	2.6×10^5	1:1000	40	1300
0	0	1:1000	0	4000*

* oil completely dispersed

TABLE 15:

A Summary of the Lowest Feasible Concentration of Brand S Required to Inhibit Emulsification Under Various Conditions

Oil Type	Temperature	Fresh Oil	24 hour weathering	121 hour weathering
Avalon J-34 Crude Oil	20°C	1:5000	1:5000	1:1000
	10°C	1:1000	Marginal @ 1:1000	Failed @ 1:1000
	0°C	oil gelled into balls		
Alberta Sweet Mixed Blend Crude Oil	20°C	1:10000	1:5000	1:1000
	10°C	1:5000	1:1000	Marginal @ 1:1000
	0°C	1:1000	D.N.T.	D.N.T.

D.N.T. = did not test

3.3.5 Effect of Slick Thickness on Surfactant Performance

Figures 20 and 21 illustrate the effect of slick thickness (150 ml = 5 mm vs. 50 ml = 1.5 mm) on the emulsification and dispersion of dosed Avalon J-34 crude oil. At a surfactant concentration of 1:10000 the thinner slick dispersed almost completely while the thicker slick gradually developed from 5 mm globules into a 60% water-in-oil emulsion over 2 hours. At 1:5000 both slicks dispersed rapidly; the 1.5 mm slick dispersed as very small droplets ($\ll$1 mm) while the 5 mm slick dispersion contained many larger droplets ($\approx$ 1 mm).

3.3.6 Effect of Mixing Energy on Surfactant Performance

Figure 22 shows the effect of mixing energy on emulsification and the performance of the surfactant. At the lower hoop oscillation rate surfactant free oil incorporates water almost as rapidly as at the higher rate, however the water drops are much larger at the lower rate than at the higher (1 to 10 mm diameter as opposed to < 1 mm). The emulsion that was formed at the lower mixing energy separated once it was removed from the test tank.

As shown in Figure 22, surfactant performance (at 1:10000) is better at the higher mixing energy level than at the lower, but that the final water content of the emulsion is the same for both. The results at 1:5000 are unusual, but duplicate runs done at 1:5000 at 150 rpm indicated that the equilibrium water content is zero and that the rise in water content shown on Figure 22 is an anomaly.

The effect of mixing energy on dispersion is quite dramatic; a decrease in hoop oscillation rate from 220 to 150 rpm results in almost an order of magnitude decrease in dispersed oil concentration (Figure 23). Two different energy types are required for dispersion, one to create droplets from a slick (in a range of sizes) and one to determine what percentage of these droplets remain dispersed and what percentage rise to recoalesce with the slick. Obviously the surfactant can only influence the first of these by reducing interfacial tensions and allowing more, smaller droplets to be produced per unit energy.

FIGURE 20: EFFECT OF SLICK THICKNESS ON SURFACTANT PERFORMANCE
EMULSIFICATION VS TIME (FRESH J-34 AT 20°C)

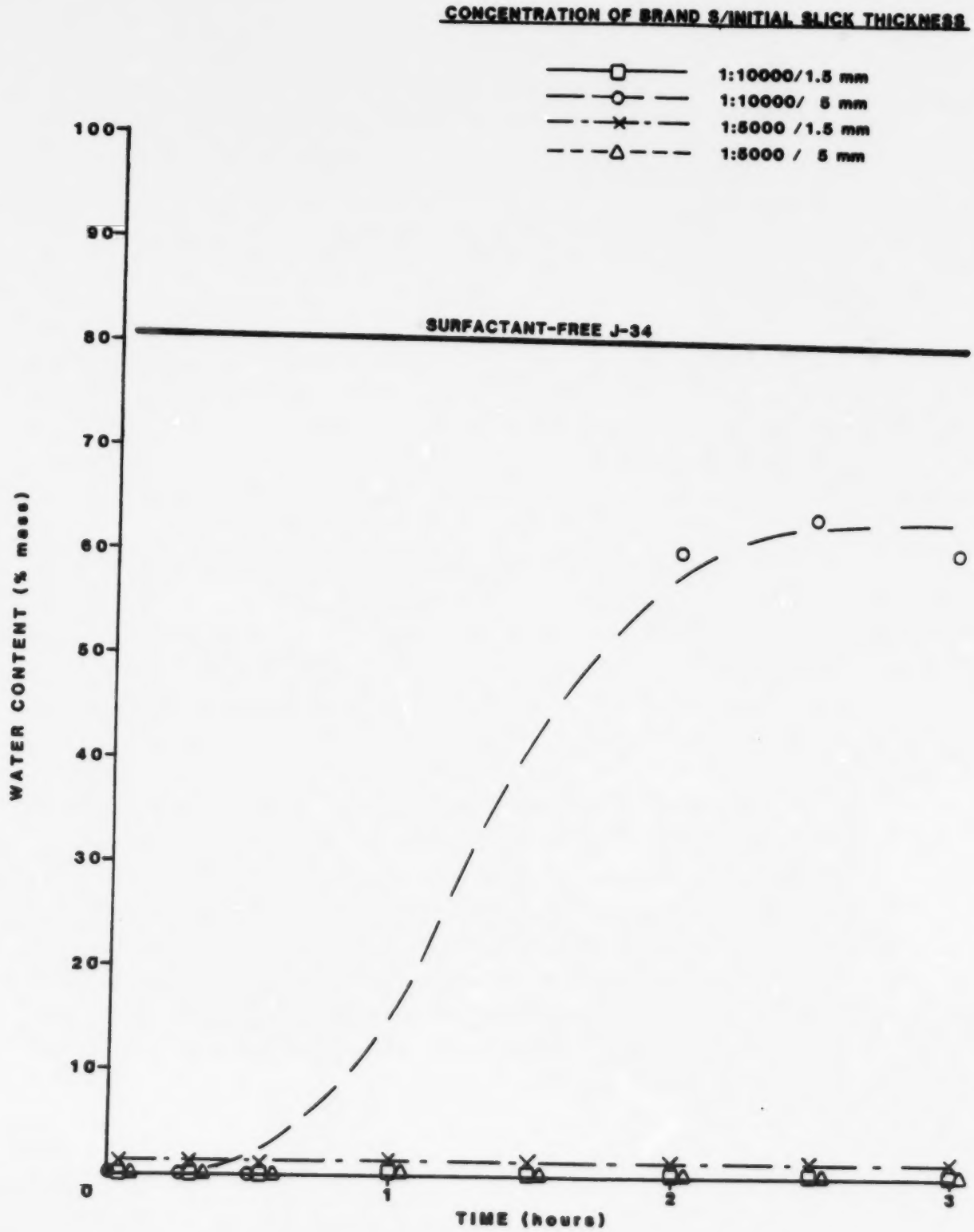


FIGURE 21: EFFECT OF SLICK THICKNESS ON SURFACTANT PERFORMANCE
DISPERSION VS TIME (FRESH J-34 AT 20°C)

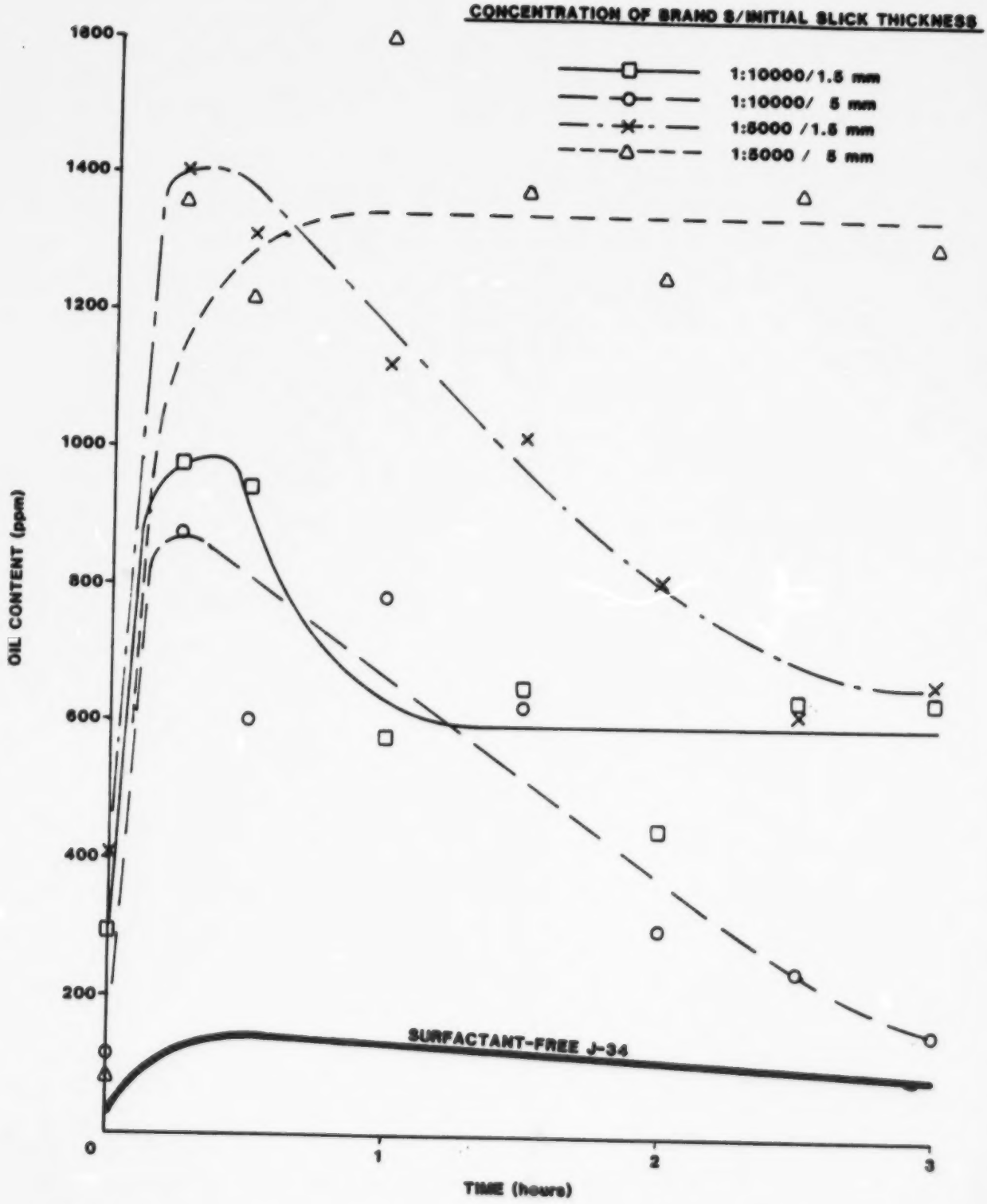


FIGURE 22: EFFECT OF MIXING ENERGY ON SURFACTANT PERFORMANCE
EMULSIFICATION VS TIME (FRESH J-34 AT 20°C)

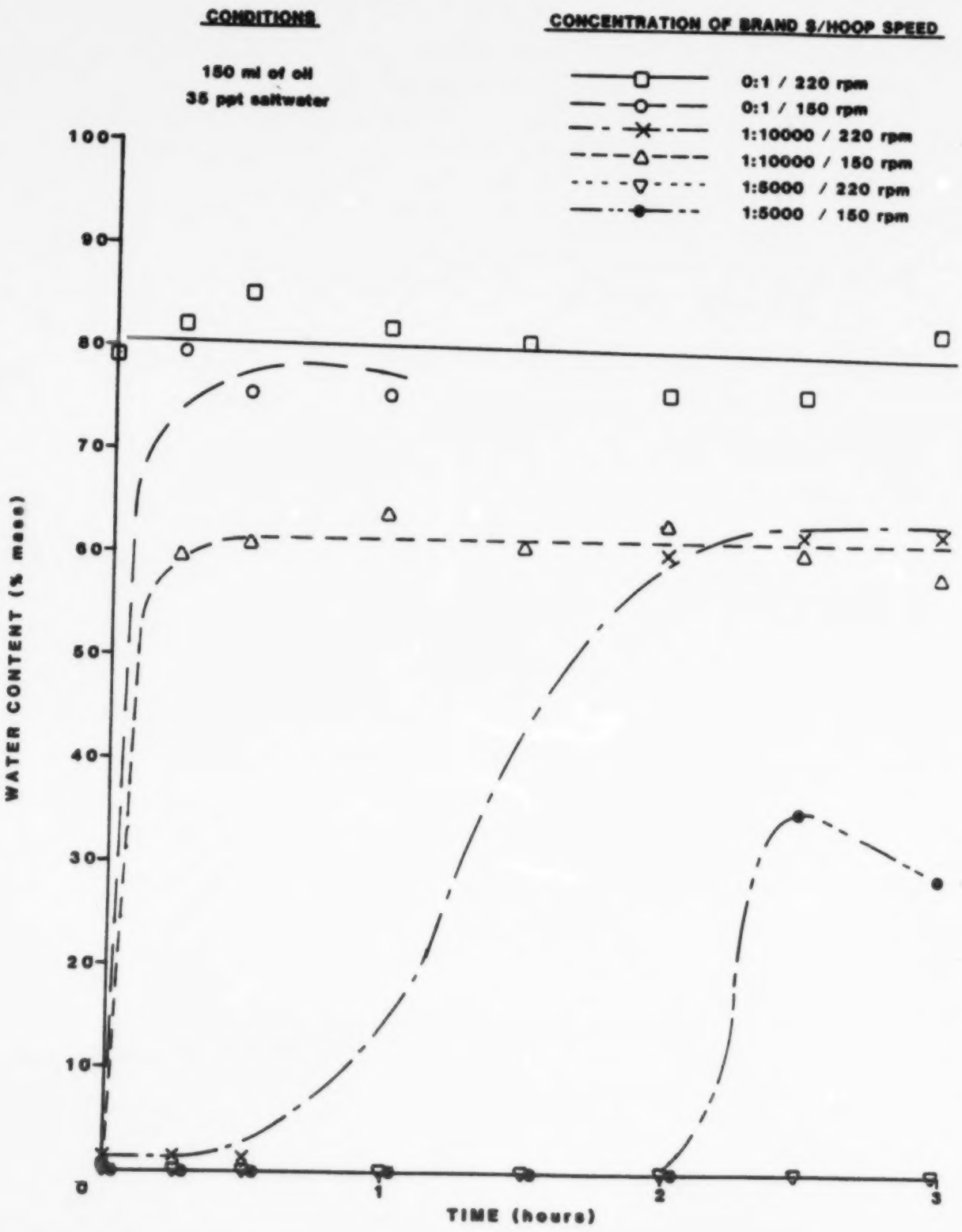
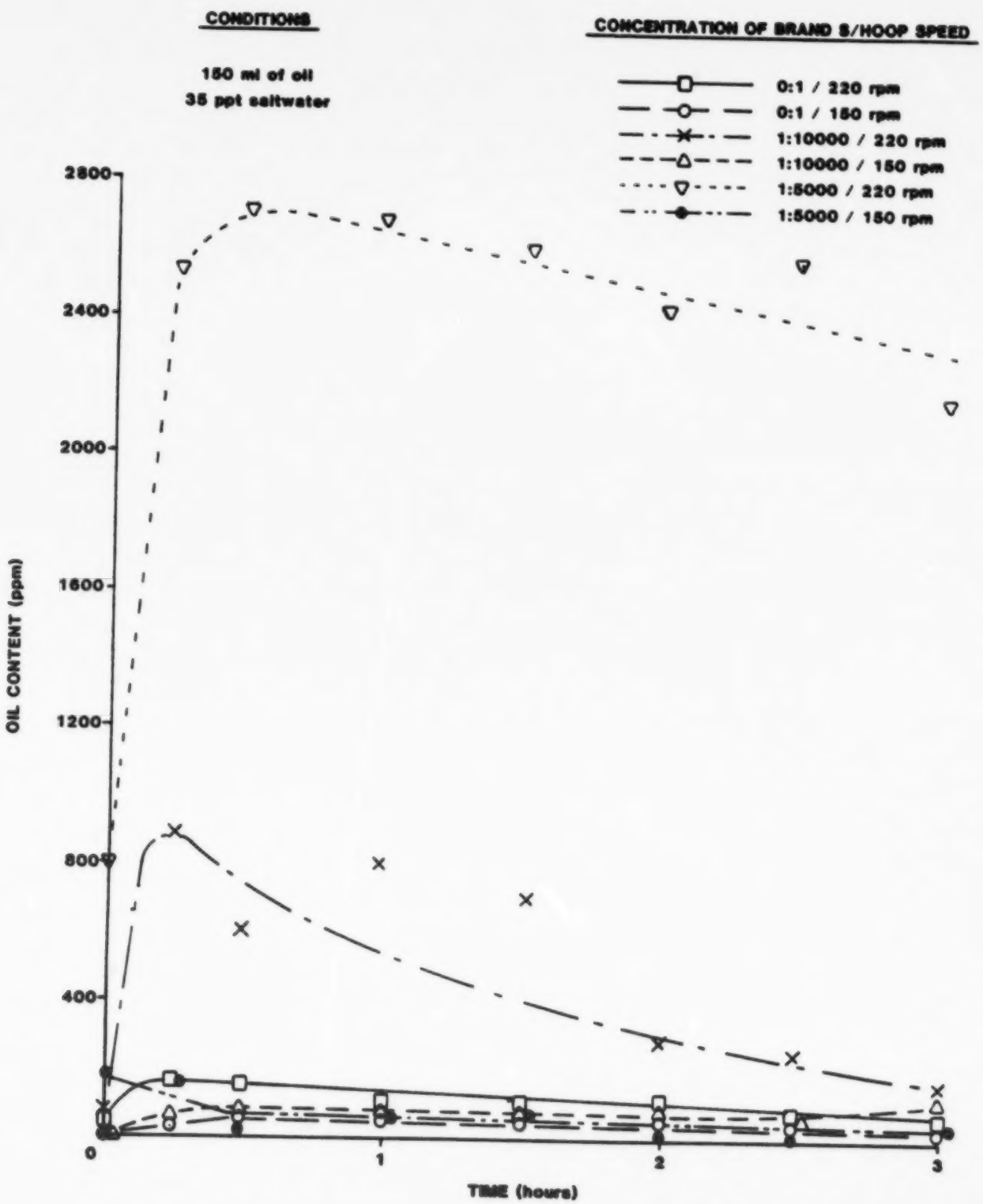


FIGURE 23: EFFECT OF MIXING ENERGY ON SURFACTANT PERFORMANCE
DISPERSION VS TIME (FRESH J-34 AT 20°C)



3.3.7 Surfactant Application Techniques

Figure 24 shows a comparison of surfactant application methods (premixed vs. dropwise or sprayed). Premixed is the most efficient technique with dropwise addition being far superior to fine-mist addition.

Figure 25 shows the dispersion results for these same tests. Spraying as a fine mist is an inefficient method of surfactant delivery for the J-34 oil.

For fresh ASMB, however, both sprayed and dropwise addition at 1:5000 resulted in complete dispersion of the fresh oil at 20°C (Figure 26). The difference between the two oils is likely related to their pour points (21°C for J-34 vs. -4°C for ASMB). The surfactant has difficulty penetrating and mixing with the J-34 while it mixes easily with the more fluid ASMB.

3.3.8 Comparison with Dispersants

Figures 27 and 28 show a comparison of the performance of Brand S vs. Corexit 9527, a state-of-the-art oil spill dispersant. A premixed concentration of 1:5000 of Brand S resulted in complete dispersion of the oil whereas the 1:5000 premixed 9527 formed a weak emulsion containing 1 mm diameter water droplets. It is not surprising that 9527 does have a slight emulsion inhibiting effect since one of its active ingredients is sodium dioctyl sulfosuccinate (Wells 1985) tested during the first phase of this study.

Figures 29 and 30 illustrate that the salinity of the water has no effect on the performance of the surfactant in inhibiting emulsification or in enhancing dispersion.

FIGURE 24: COMPARISON OF SURFACTANT APPLICATION METHODS
EMULSIFICATION VS TIME (J-34 AT 20°C)

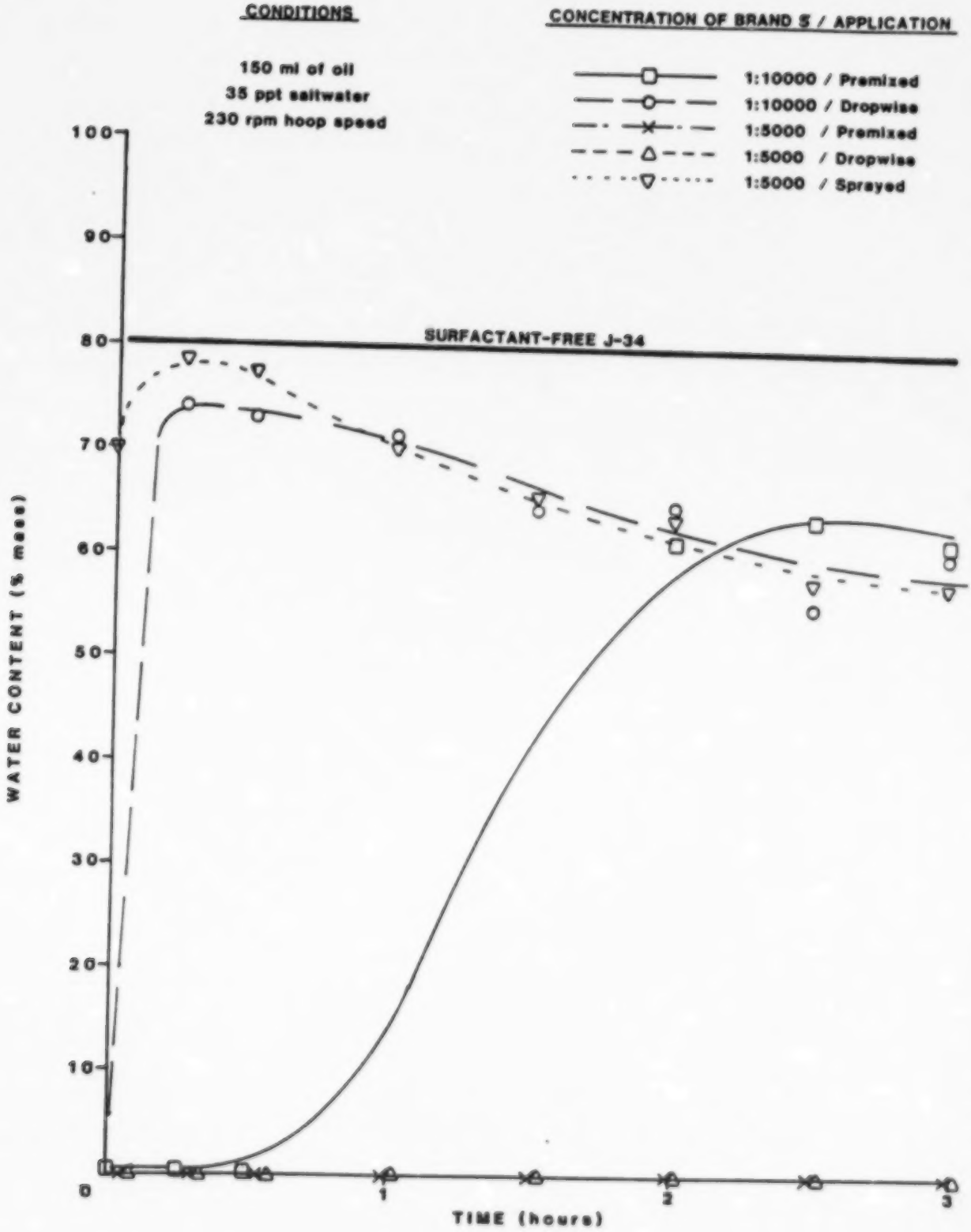


FIGURE 25: COMPARISON OF SURFACTANT APPLICATION METHODS
DISPERSION VS TIME (J-34 AT 20°C)

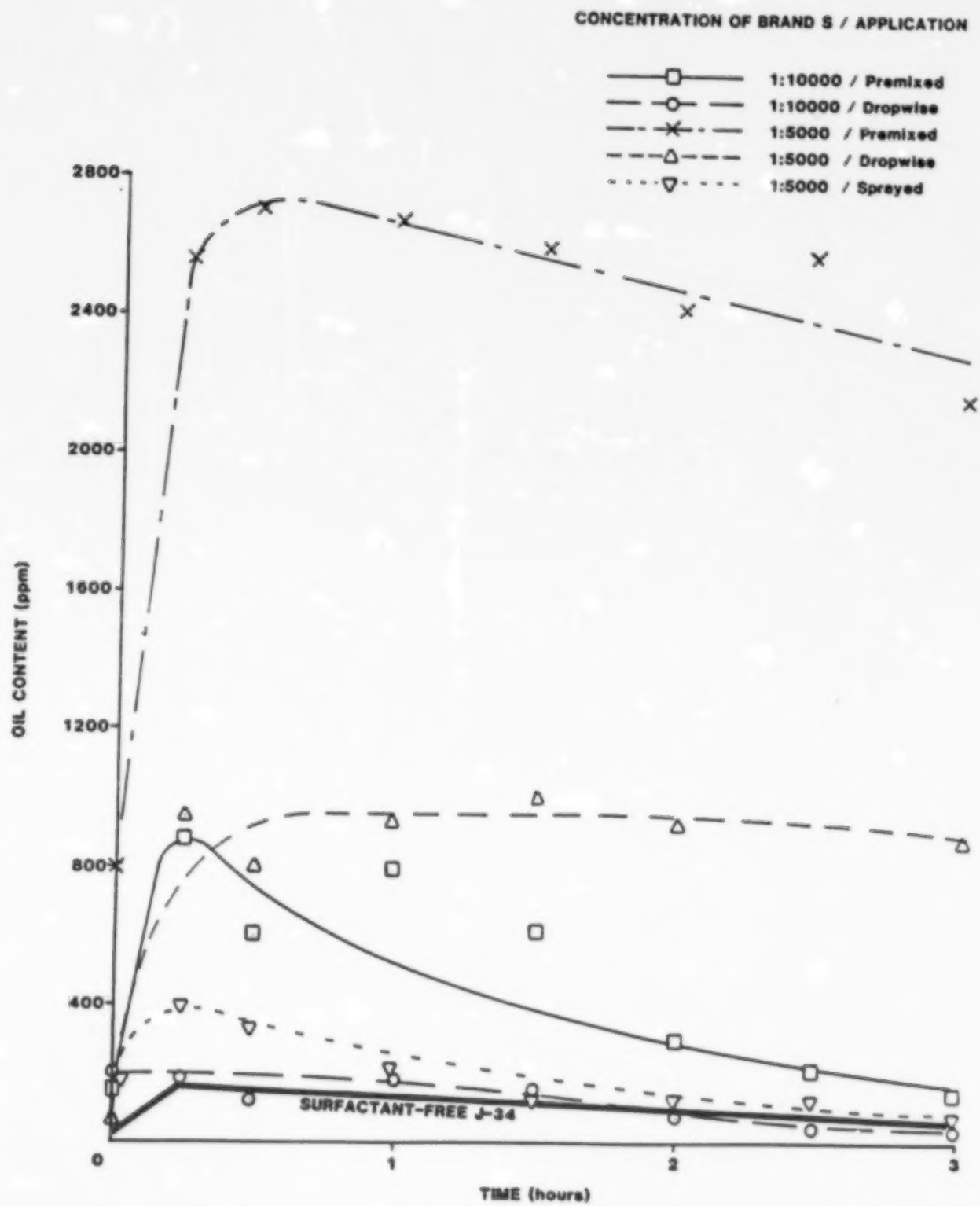


FIGURE 26: COMPARISON OF SURFACTANT APPLICATION METHODS
DISPERSION VS TIME (ASMB AT 20°C)

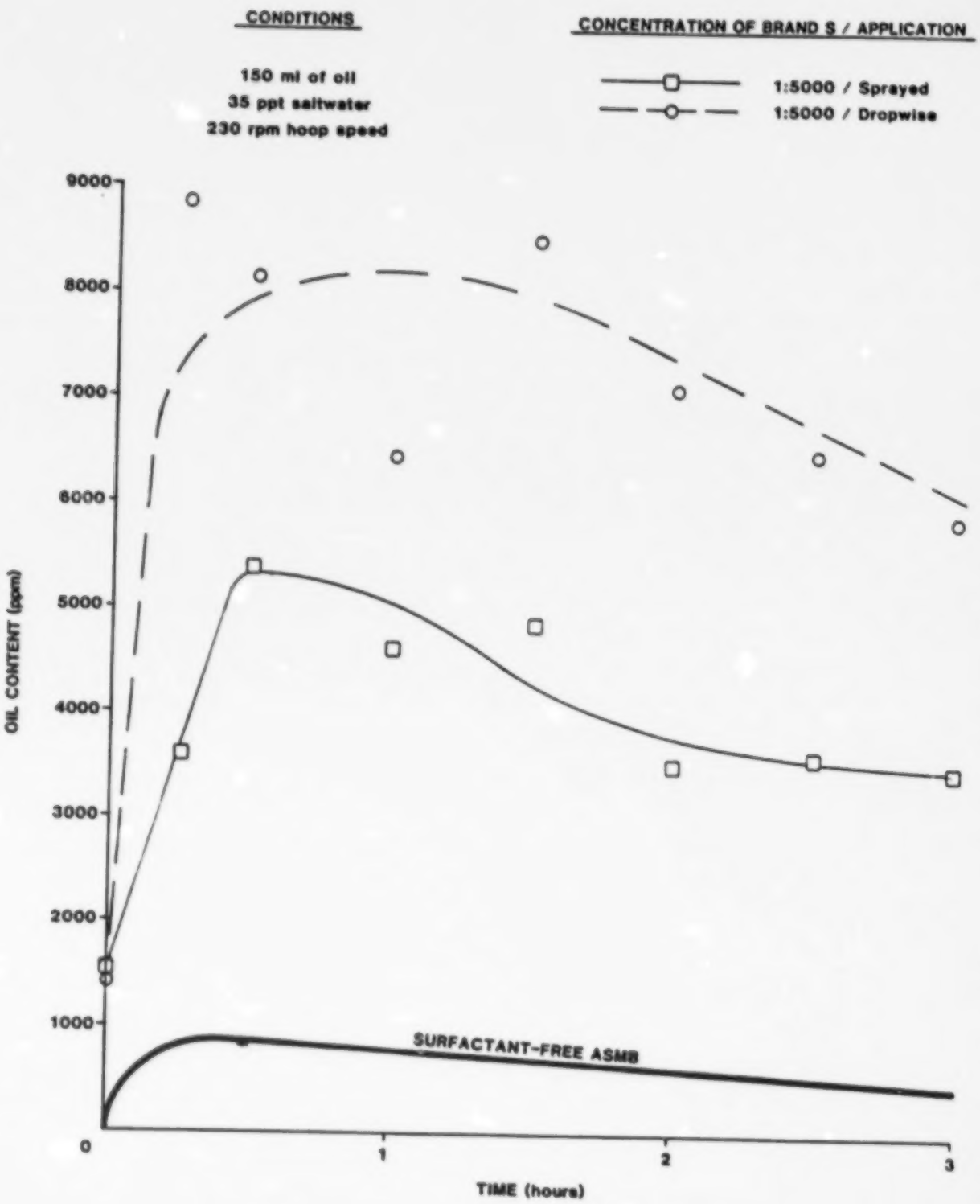


FIGURE 27: COMPARISON OF SURFACTANTS
EMULSIFICATION VS TIME (J-34 AT 20 °C)

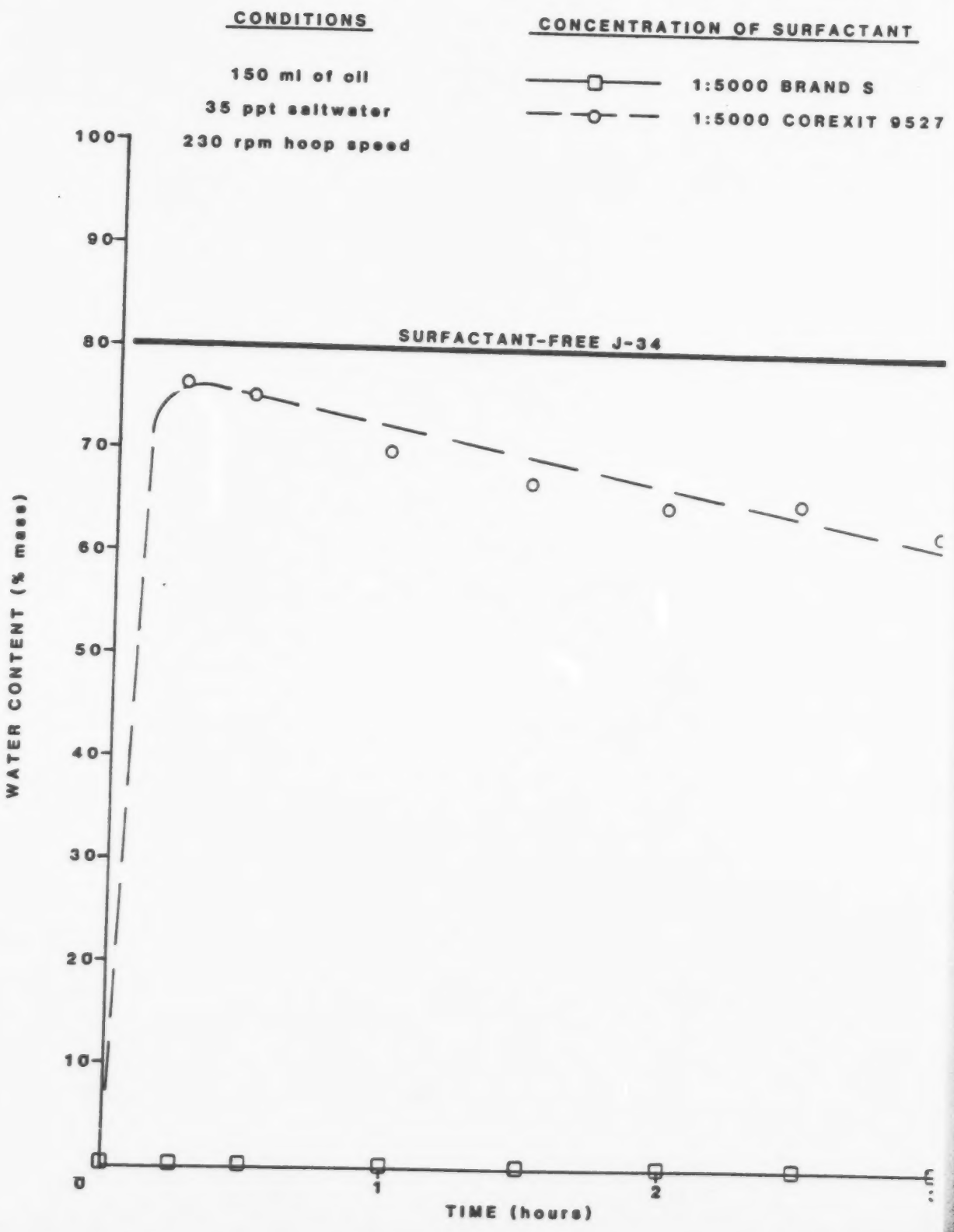


FIGURE 28: COMPARISON OF SURFACTANTS
DISPERSION VS TIME (J-34 AT 20°C)

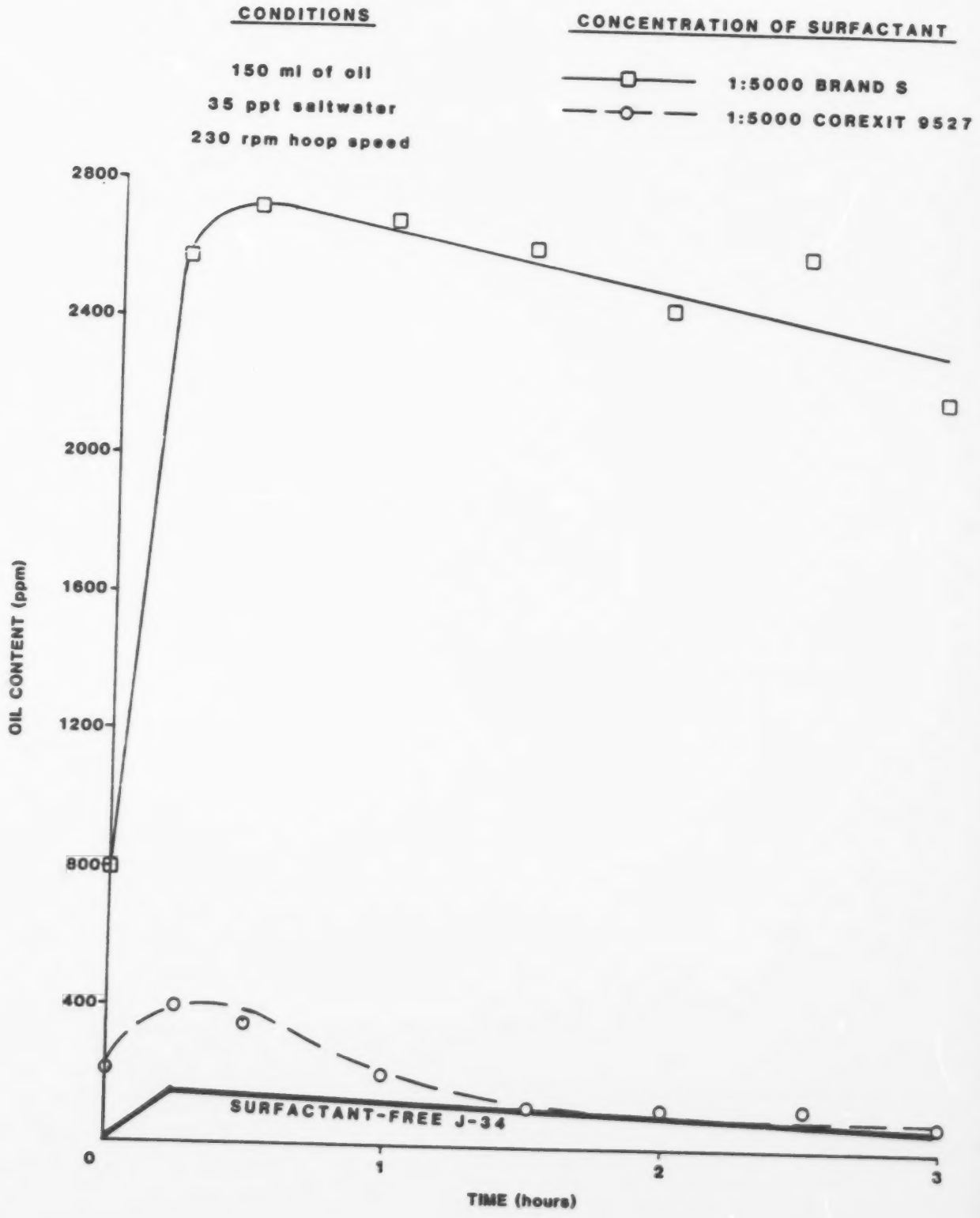


FIGURE 29: EFFECT OF WATER SALINITY ON SURFACTANT PERFORMANCE
EMULSIFICATION VS TIME (FRESH J-34 AT 20 °C)

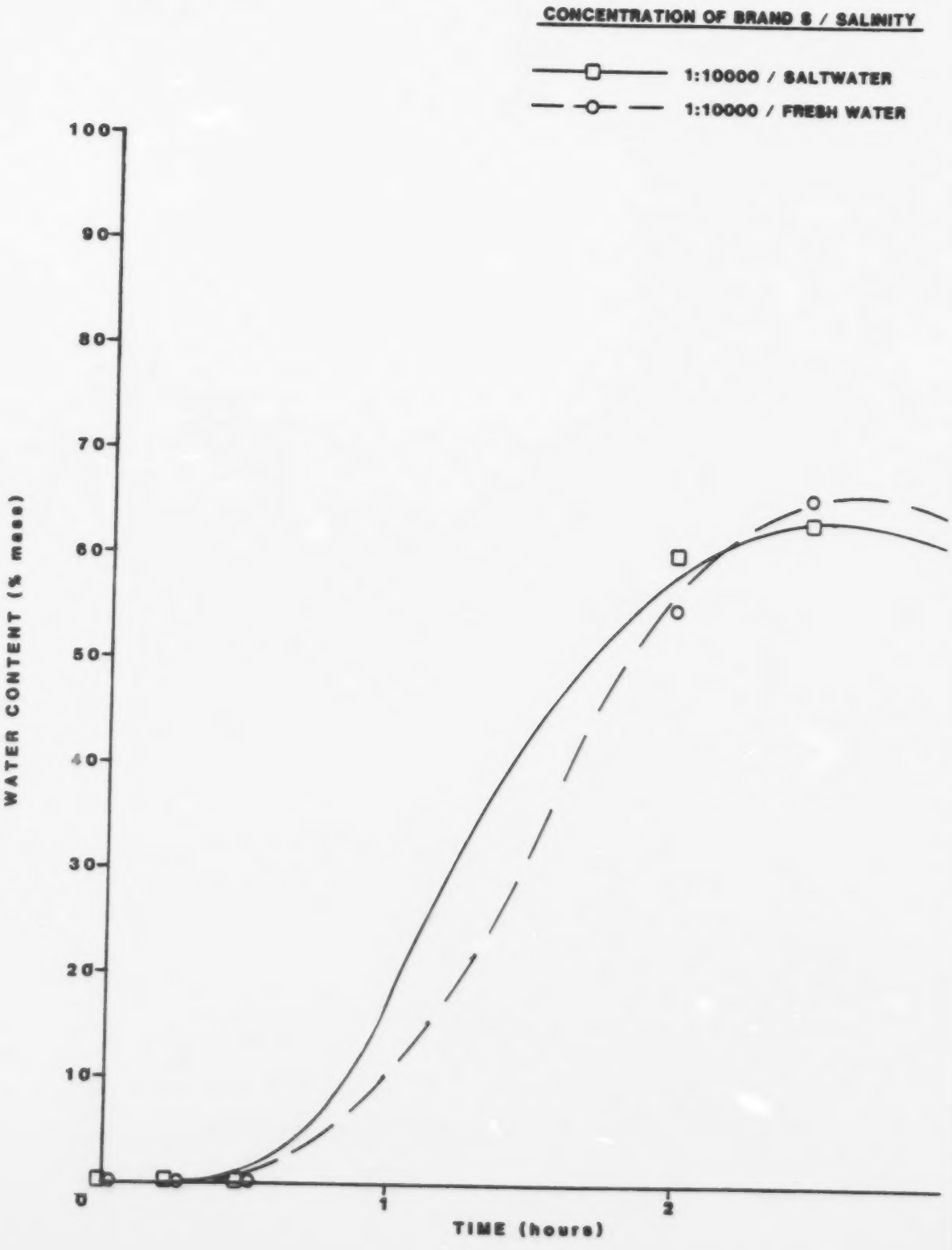
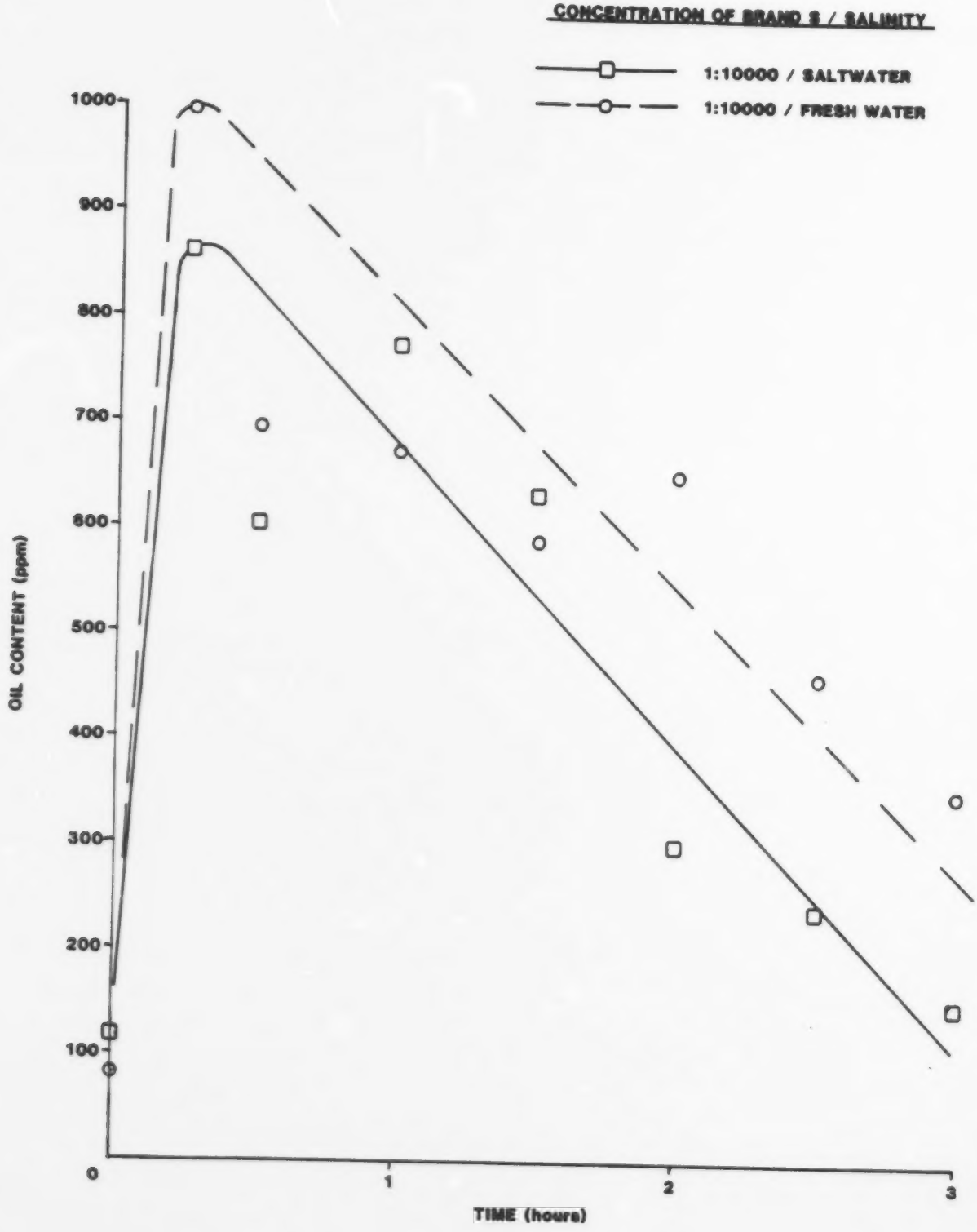


FIGURE 30: EFFECT OF WATER SALINITY ON SURFACTANT PERFORMANCE
DISPERSION VS TIME (FRESH J-34 AT 20°C)



3.4 SUMMARY AND CONCLUSIONS

The surfactant, Brand S, has been shown to be an effective emulsion inhibitor at very low concentrations. Two factors seem to be the prime determinants of its performance, oil viscosity and surfactant concentration. As an oil weathers and/or cools more surfactant is required to maintain the oil in an unemulsified state. It seems likely that this is due to the increased viscosity of the continuous oil phase, since viscosity is the only property that changes dramatically over the ranges of temperature and weathering investigated. It is unclear what specifically reduces the effectiveness of the surfactant as viscosity of the oil increases; it is probably a combination of reduced mobility of the chemical in the oil, reduced drainage rates of oil between closely approaching water droplets and lower settling rates of water droplets. The precipitation of waxes or other interface stablizing compounds in the oil at oil-water interfaces, as temperatures decrease, may also be a contributing factor.

It is interesting to note that the above analysis does not hold for situations where the ambient temperature is much less than the pour point of the oil. Results show that when the temperature is about 20°C below the pour point, the oil no longer emulsifies but rather becomes highly viscous and takes the form of non-coalescing, semi-solid, smooth, spherical particles.

One unexpected benefit of adding the emulsion inhibiting chemical to the oil is that it greatly enhances dispersion rates, even at very low concentrations. Complete dispersion of the oil was noted for concentrations as low as 1 part Brand S in 5000 parts oil. At these concentrations, a conventional dispersant produced little enhancement.

Four regimes of emulsion prevention can be identified with respect to inhibitor concentration. First, with no inhibitor present the oil rapidly forms a stable, highly viscous, brown emulsion. Second, at certain low concentrations of inhibitor the oil still emulsifies into a black coloured product but the

entrained water droplets are larger and the water content, viscosity and stability of the emulsion are lower than the emulsion formed with the inhibitor-free oil. Third, at larger inhibitor concentrations, emulsion formation is prevented and the oil remains on the surface as a black, relatively non-viscous layer. At this stage, dispersed oil concentrations are about two or three times higher than the case for untreated oil. Finally, at still higher inhibitor concentrations the slick is completely dispersed into the water phase.

The effectiveness of the surfactant is also related to mixing energy; the higher the mixing energy the more efficient the chemical is. With no surfactant present, higher mixing energies result in more quickly formed and more stable emulsions. At borderline surfactant concentrations higher mixing energies result in a greater delay in the emulsification process, but no effect on the final equilibrium water content is apparent. At higher concentrations no effect of mixing energy is apparent although dispersed oil concentrations are elevated at higher mixing levels.

In summary, it is apparent that the surfactant, Brand S, has two effects on emulsifiable oils. The first is a reduction in oil-water interfacial tension which promotes the dispersion of oil droplets in water, and the second is some (as yet unknown) effect on the water droplets or the stabilizing film surrounding them which greatly enhances recoalescence of the entrained drops. This latter effect inhibits or prevents emulsion formation. For actual oil spills at sea it is easy to surmise that both effects working in tandem would promote the complete dispersion of the oil over time. Further testing of the chemical to measure its dispersing capabilities and further testing in a larger, more realistic mixing tank are needed to determine whether this is indeed the case. These are the subjects of the next two chapters.

4.0 DISPERSANT EFFECTIVENESS TESTING

Since the chosen emulsion inhibitor unexpectedly proved in the small-scale testing to significantly promote dispersion as well as inhibit emulsification it was decided to more fully test the effectiveness of the chemical as a dispersant.

4.1 PURPOSE

The goal of this phase of the study was to determine the effectiveness of Brand S as a dispersant and the effect of solvent and temperature on its performance.

4.2 METHODS

The tests were conducted in an MNS dispersant effectiveness apparatus according to Environment Canada standard procedures (Environment Canada 1984) using EPS Standard ASMB crude oil. The tests were conducted in the cold room at Environment Canada's River Road Environmental Technology Centre.

The inhibitor was diluted 1:100 in solvent for most of the runs to make possible even, dropwise addition of small amounts of the chemical. Blanks (solvent only) were run to assess the effect of the solvent. Control runs were also performed with no inhibitor or solvent added. The test matrix included the following parameters:

* four temperatures (0, 5, 10 and 15°C)
* one energy level (30 cm H_2O pressure drop)
* four inhibitor:oil ratios (1:500, 1:1000, 1:2000 and 1:4000)
* four solvent types (neat, toluene, naptha and acetone)
* two application methods (premixed or dropwise)

In addition two comercially available dispersants (Corexit 9527 and 9550) were tested under identical conditions (with dispersant:oil ratios of 1:20, 1:50 and 1:100) with and without preaddition of the inhibitor. These tests were conducted to determine if the inhibitor had any effect on conventional dispersant performance.

4.3 RESULTS AND DISCUSSION

Table 16 shows the results of the tests at an inhibitor:oil ratio of 1:500. (Repeatability of the MNS test is within 5 percent.) The blanks to assess natural dispersion are shown at the far right; not shown are the solvent only blanks at 15°C which resulted in dispersions of 7.5, 10 and 9% respectively for toluene, naptha and acetone premixed with the oil at 1:5 (the volume of solvent used to get a 1:500 inhibitor-to-oil ratio).

The results show that, at 10 and 15°C the inhibitor is a surprisingly effective dispersant; as the temperature decreases below 10°C, however, its effectiveness declines dramatically. In terms of application method and solvent, premixed/neat gives the best results. At 15°C 1:500 in toluene premixed seems to give a better result; this may be the result of an experimental error or a synergistic effect between the inhibitor and toluene (toluene alone at the same volume ratio does not increase dispersion). Experimental error is the most likely reason since the result is not repeated at 10°C. Runs using naptha as a solvent consistently yielded the poorest results.

Figures 31 and 32 show the effect of inhibitor dose on dispersion at 15° and 10°C respectively. The curves for 15°C indicate that the inhibitor reaches a critical micelle concentration above which the addition of more surfactant has little or no further effect. At this temperature, at dose rates of 1:1000 or greater, there is little difference between premixed neat and dropwise addition in a solvent. At 10°C significant differences become apparent. The neat premixed case still seems to reach a critical micelle

TABLE 16

DISPERSANT EFFECTIVENESS OF BRAND "S"

(Percent Dispersed)

I/O Solvent Application	1:500 neat premixed	1:500 toluene premixed	1:500 toluene dropwise	1:500 naptha premixed	1:500 naptha dropwise	1:500 acetone premixed	1:500 acetone dropwise	blank
Temperature (Deg C)								
0	3	4		3		3		3
5	9	8		7		4		4
10	48	35	33	26	15	14	8	6
15	68	79	69	46	52	72	61	10

Notes: I/O is the inhibitor to oil ratio

Inhibitor was diluted 1 to 100 in the solvents

Premixed: oil and inhibitor are mixed together and then discharged onto the water surface

Dropwise: inhibitor is added to the oil surface in droplet form from an Eppendorf pipette

FIGURE 31: EFFECTIVENESS OF BRAND S AS A DISPERSANT AT 15°C

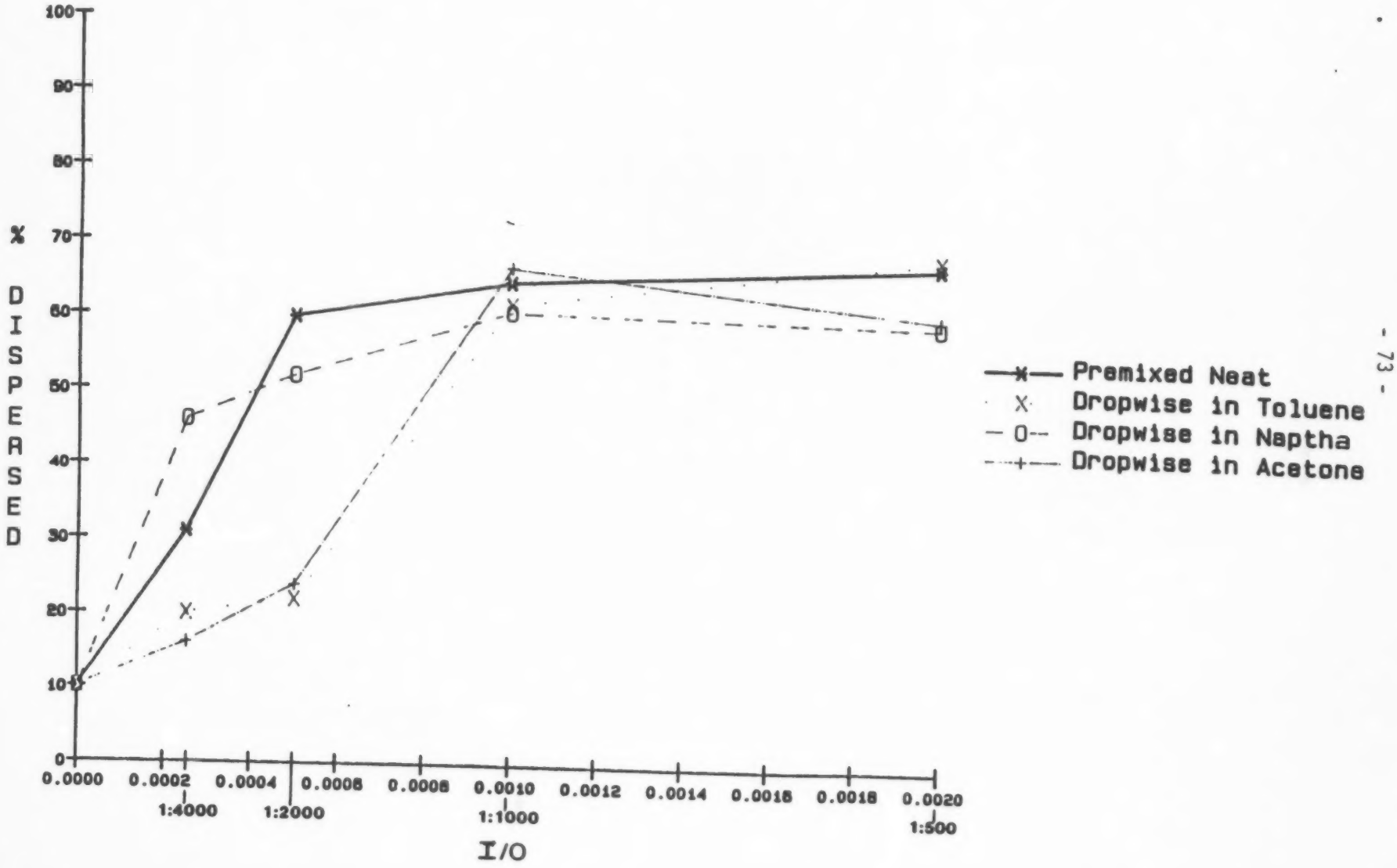
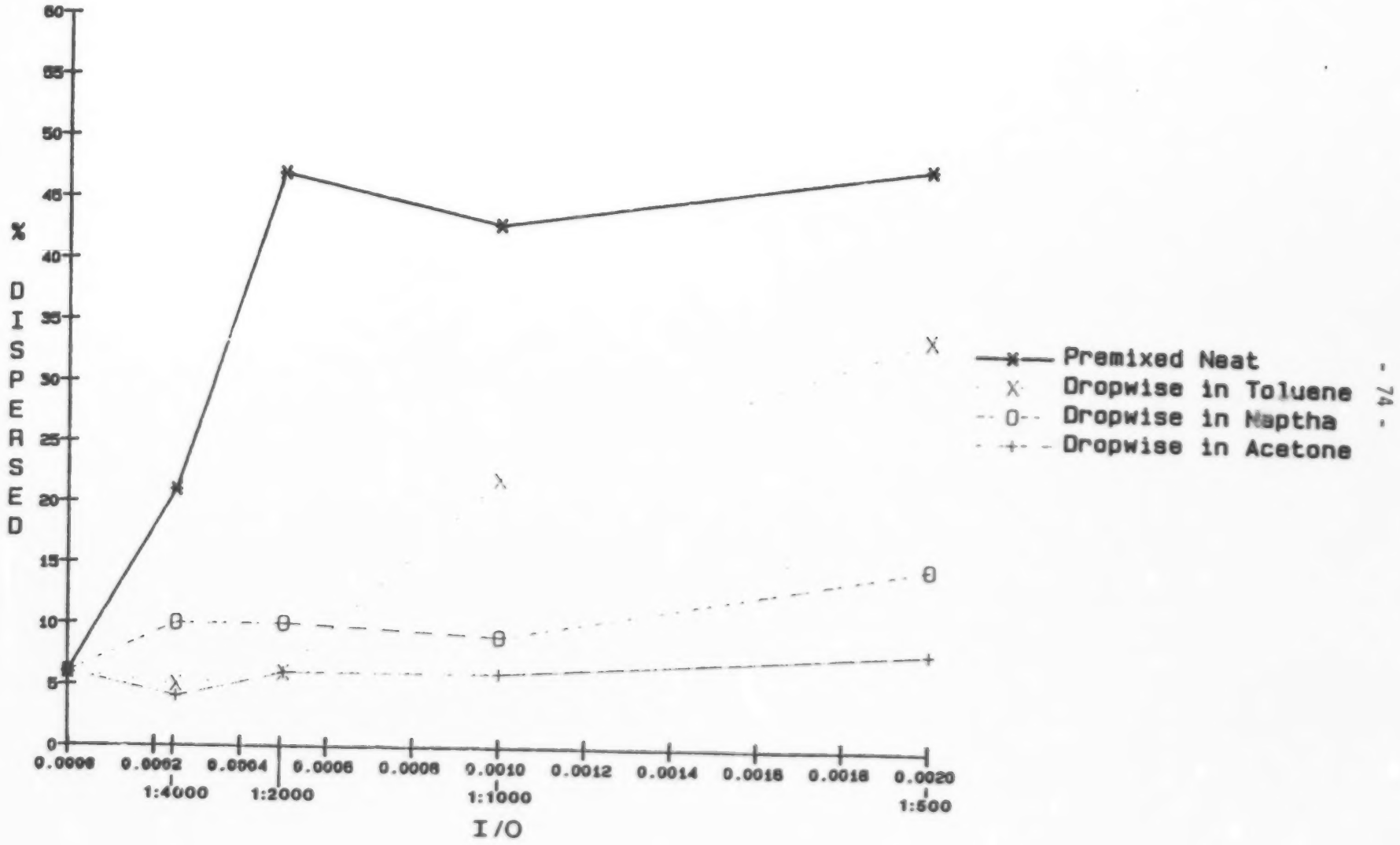


FIGURE 32: EFFECTIVENESS OF BRAND S AS A DISPERSANT AT 10°C



concentration but the solvent cases do not. Overall, dispersant efficiency at 10°C (neat, premixed) is only two-thirds that at 15°C. Tests at different doses were not conducted at lower temperatures since the inhibitor did not significantly promote dispersion at dose rates of 1:500 at 5° and 0°C.

Figure 33 illustrates the effect of temperature on the enhancement of dispersion by Brand S. As with emulsion inhibition 10°C seems to be a critical temperature. Unlike emulsion inhibition the phenomenon cannot solely be linked with oil viscosity effects as evidenced by the different slopes of the dosed, natural dispersion curve vs. the Corexit 9527 @ 1:20 curve, both of which rise only slightly with increasing temperature. It may be that the mobility of the surfactant in the oil is a contributing factor.

Figure 34 shows a comparison of temperature effects on dispersant effectiveness for Corexit 9527 at 1:20, Corexit 9550 at 1:20 and 1:100 and Brand S at 1:500, 1:1000, 1:2000 and 1:4000. All chemicals were added dropwise. For a given surfactant, as the concentration decreases, above the critical micelle concentration, the slope of the effectiveness vs. temperature curve increases. This implies that the migration of surfactant molecules within the oil to freshly created interface as the oil droplets split may be limiting the effectiveness of the chemicals.

Tables 17 and 18 show the results of tests conducted to determine the effect of the inhibitor on conventional dispersant effectiveness. The presence of Brand S consistently resulted in a slight improvement in the effectiveness of Corexit 9527 and 9550 at all temperatures and concentrations tested.

FIGURE 33: DISPERSANT EFFECTIVENESS OF BRAND S AT I/O = 1:500
AS A FUNCTION OF TEMPERATURE

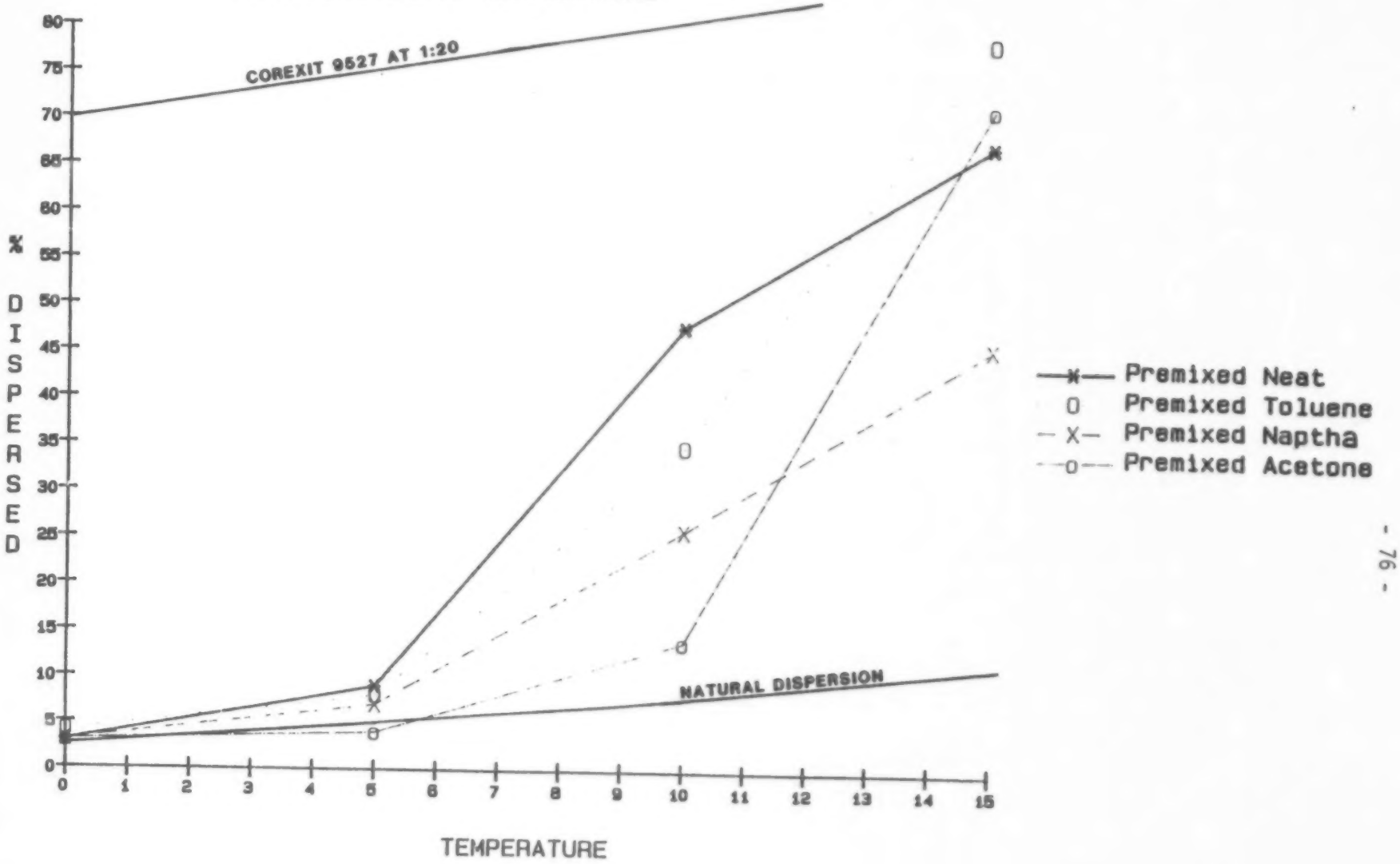


FIGURE 34: COMPARISON OF TEMPERATURE EFFECTS ON DISPERSANT EFFECTIVENESS

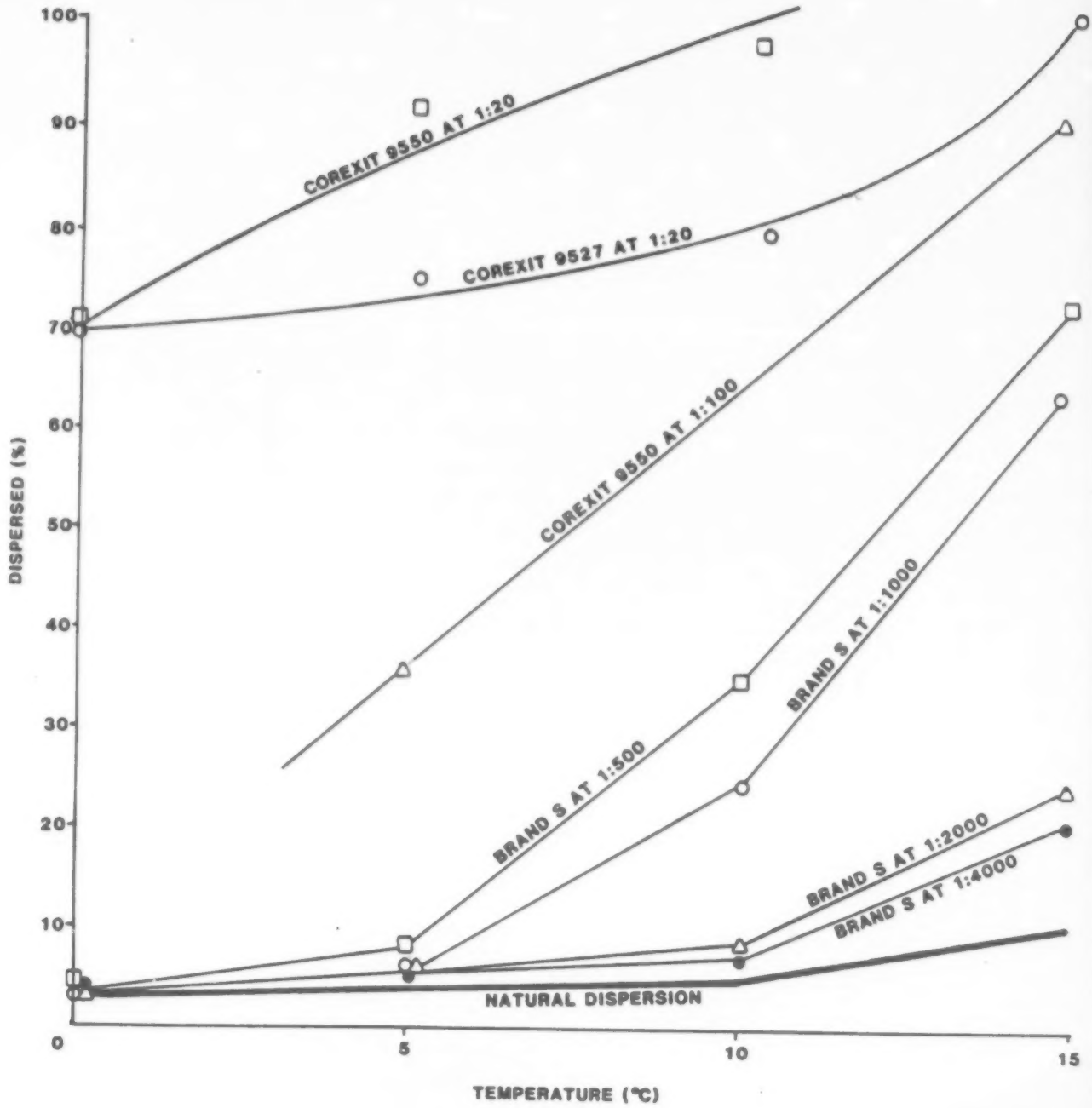


TABLE 17:

EFFECTIVENESS OF COREXIT 9527 AND BRAND "S" COMBINED
(Percent Dispersed)

TEMPERATURE (DEG C)	Dispersant Only	Dispersant and Brand "S"
0	73	70
	69	
5	75	88
	71	
10	80	91
	76	80 (I/O= 1:4000)
15	98	--

Notes: Dispersant was applied to the oil surface in droplet form from an Eppendorf Pipette.

Dispersant to oil ratio was 1:20.

Oil and inhibitor were premixed together and then discharged onto the water surface.

I/O is the inhibitor to oil ratio which, unless is otherwise stated, was 1:500.

TABLE 18:

EFFECTIVENESS OF COREXIT 9550 AND BRAND "S" COMBINED
(Percent Dispersed)

TEMPERATURE (DEG C)	Dispersant Only (Dispersant to Oil)	Dispersant and BRAND "S"
0	69 (1:20)	83
5	91 (1:20)	--
	76 (1:50)	81
	36 (1:100)	37
10	96 (1:20)	--
15	88 (1:100)	93

Notes: Dispersant was applied to the oil surface in droplet form from an Eppendorf Pipette.

Dispersant to oil ratios appear in brackets.

Oil and inhibitor were premixed together and then discharged onto the water surface.

Inhibitor to oil was 1:500.

4.4 SUMMARY AND CONCLUSIONS

The results show that Brand S in low concentrations dramatically enhances dispersion rates at temperatures above 10°C. Results are less dramatic at temperatures below 10°C. In addition, when used in conjunction with conventional dispersants Brand S seems to enhance the effectiveness of the dispersants, but only slightly. As might be expected the effectiveness of Brand S improves as its concentration increases and when the product is premixed into the oil rather then added dropwise during the experiment.

5.0 MESO-SCALE EFFECTIVENESS TESTS

5.1 PURPOSE

The goal of this series of tests was to evaluate the effectiveness of the emulsion inhibitor in a larger system over longer periods of time, and in a more realistic energy environment characteristic of lower sea states.

5.2 METHODS

The tests were conducted in a wind/wave tank (Plate 5) 11 m long, 1.1 m wide and 1.55 m high. Ten thousand litres of fresh water (a depth of 0.85 m) and two litres of oil were used in each test. Fresh water rather than salt water was used for these runs to simplify test preparations. Figures 29 and 30 show that water salinity had no effect on inhibitor performance.

The test matrix was as follows:

* two crude oils (Avalon J-34 and Alberta Sweet Mixed Blend)
* four inhibitor-to-oil dose rates (0:1, 1:10,000, 1:5000 and 1:1000)
* two temperatures (about 10^{o}C and 15^{0}C)
* two combinations of wind and wave height (1m/s and 17 cm (energy level 1) vs 2m/s and 20 cm (energy level 2)).

The wind opposed the direction of wave travel in order to hold the slick in the centre of the tank.

The test procedure was as follows:

1. fill the tank with 10,000 L of fresh water; adjust temperature to 10^{o} or 15^{0}C by adding hot water
2. set the fan and wave generator to achieve either energy level 1 (1m/s wind, wave generator stoke of 25 cm at 0.9 Hz) or energy level 2 (2m/s wind, wave generator stoke of 25 cm at 1 Hz)

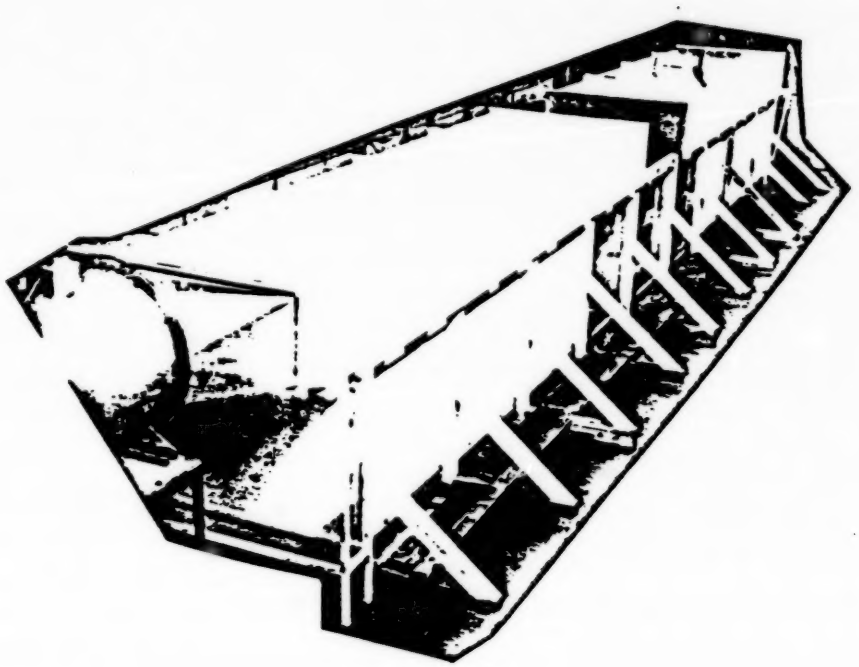


PLATE 5 - WIND/WAVE TANK

3. gently pour 2 L of the test oil premixed with the inhibitor diluted 1:10 in toluene onto the water at the centre of the tank
4. take water column samples (100 ml) (from top, middle and bottom parts) and slick samples (using a plexiglass slide to adsorb emulsion) at 15, 30, 45, 60, 90 and 180 minute intervals (some tests were run as long as 24 hours)
5. analyse the oil content of water and water content of oil (as specified for the hoop tank tests - see Section 3.2.3)
6. after each run, turn off wave generator, allow oil to resurface and wipe and skim up any surface oil

The tank was not refilled for each run because of the time involved in heating tap water from 2°C to the desired temperature. The tests were configured in groups by temperature, energy level and surfactant concentration. For a given temperature and energy level the tank was cleaned and the different concentrations tested in increasing order (i.e., undosed oil first, 1:10,000 second, 1:5000 third and 1:1000 last) so that any inhibitor remaining after removing the oil would not interfere with the next, higher dosage test.

5.3 RESULTS AND DISCUSSION

Table 19 gives a summary of the conditions and results of the tests.

Figure 35 shows the effect of inhibitor dosage on the water uptake of J-34 oil at 15°C and energy level 1. With no inhibitor present the oil rapidly takes up water to form balls of emulsion about 5 cm in diameter, surrounded by a thin sheen of oil. The oil samples were taken from these balls. Oil that drifted to the end of the tank was heavily emulsified into a brown mousse by the action of breaking waves. Though dispersion samples were taken for all runs, only in two cases of twenty three were dispersed oil concentrations above the lower limit of detectability of 10 ppm found. As such, no reliable data on the enhancement of dispersion are available for most of the runs.

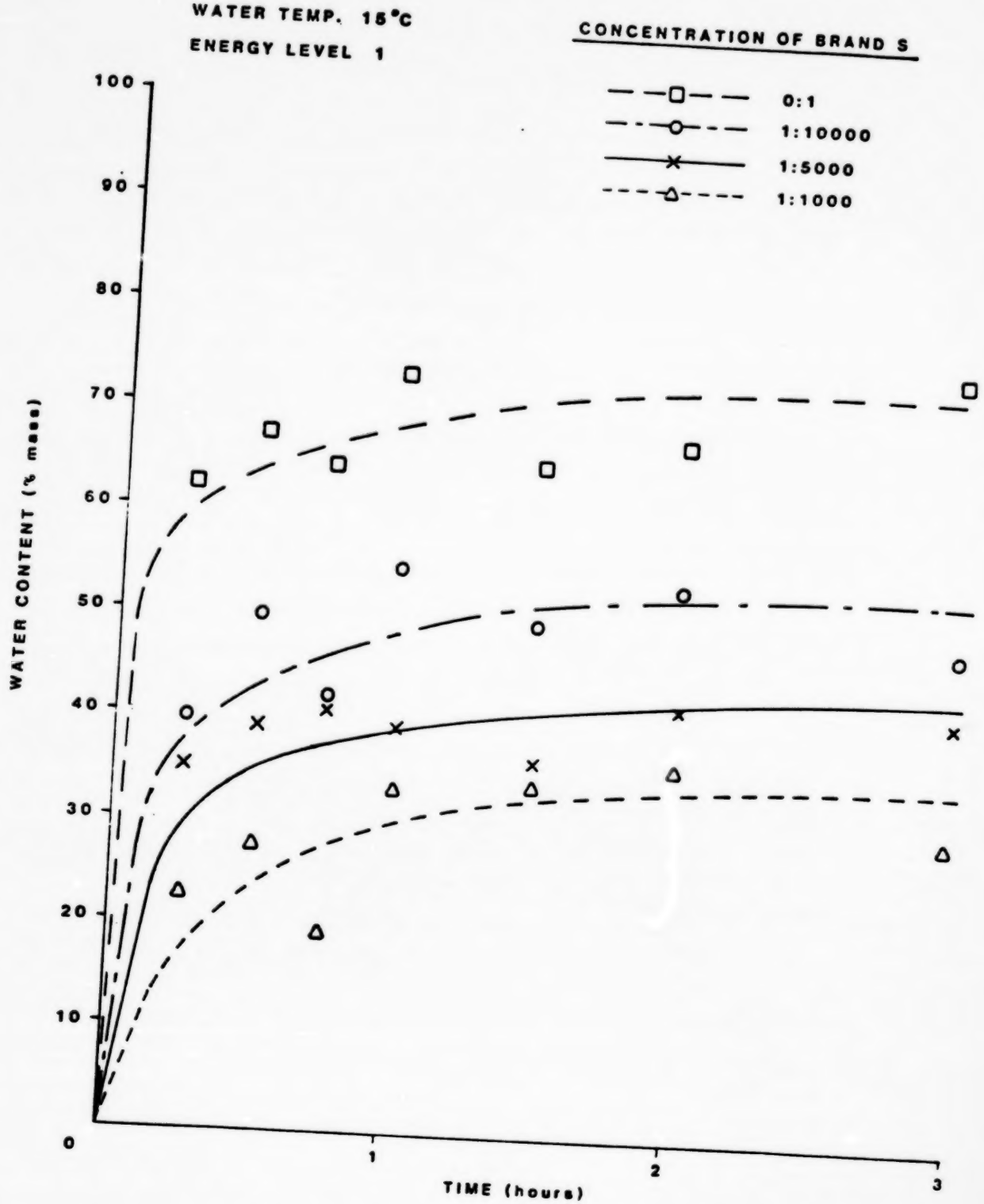
TABLE 19

SUMMARY OF WIND/WAVE TANK TRIALS

RUN	WATER TEMP (°C)	ENERGY LEVEL	OIL TYPE	SURFACTANT TYPE	SURFACTANT: OIL CONCENTRATION	FINAL EMULSION WATER CONTENT (%)
1	15	2	J-34		0:1	65
2	15	1	J-34		0:1	70
3	15	1	J-34	Brand S	1:10,000	50
4	15	2	J-34	Brand S	1:10,000	45
5	15	1	J-34	Brand S	1:5000	40
6	15	2	J-34	Brand S	1:5000	36
7	15	2	J-34	Brand S	1:1000	30
8	15	1	J-34	Brand S	1:1000	35
9	10	1	J-34		0:1	73
9A	10	2	J-34		0:1	70
10	10	1	J-34	Brand S	1:10,000	45
11	10	2	J-34	Brand S	1:10,000	45
12	10	1	J-34	Brand S	1:5000	40
13	10	2	J-34	Brand S	1:5000	40
14	10	1	J-34	Brand S	1:1000	37
15	10	2	J-34	Brand S	1:1000	35
16	10	1	ASBM		0:1	68
17	15	1	ASBM		0:1	65
18*	15	1	ASBM	Brand S	1:1000	62
23*	15	1	J-34	Brand S	1:1000	50

* 24 hour run

FIGURE 35: EMULSIFICATION VS TIME (J-34)

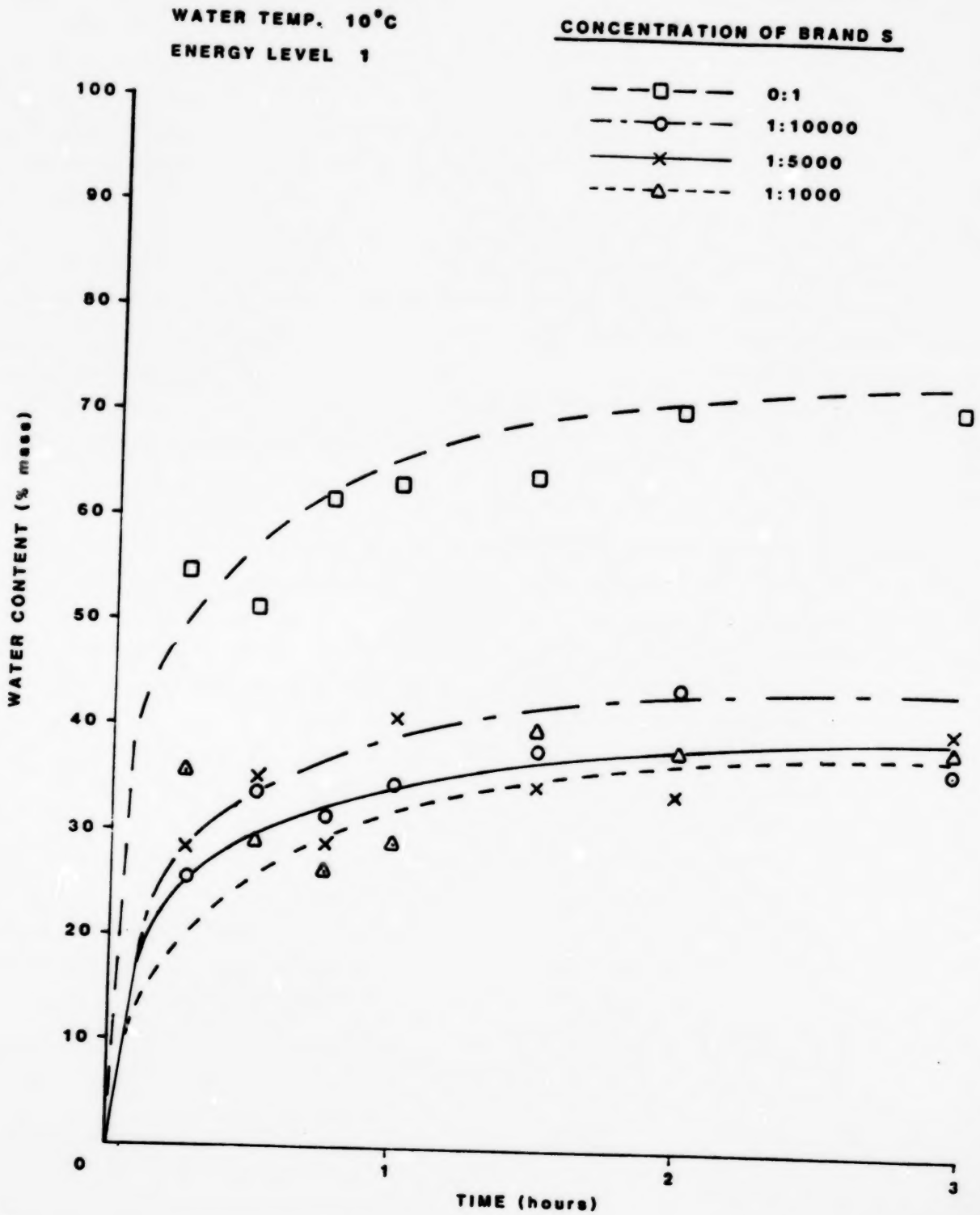


As the surfactant dose increased emulsification was inhibited more effectively. At 1:10,000 the water content was reduced to about 50% and the emulsion was in the form of balls about 2.5 cm in diameter with about 250 to 300 balls per square metre on the water surface.

At a 1:5000 dose of inhibitor the water content was reduced to about 40%. The oil took the form of 2 cm diameter balls with about 300 to 400 per square metre. No dispersion was evident or detected. At 1:1000 most of the oil remained as a coherent slick about 2-3 mm thick with a water content of only 30%. Dispersed oil concentrations were measured at approximately 20 to 30 ppm, a noticeable increase over the previous runs.

Figure 36 shows the same tests conducted at 10°C. The appearance of the undosed slick was identical to that at 15°C and both achieved the same water content (70%). The effectiveness of the surfactant at 1:10,000 was seemingly better at 10°C than at 15, though with a margin of error in water contents of 8% this may not be a real difference. Certainly the performance of the surfactant at doses 1:5000 and 1:1000 at 10°C is indistinguishable from that at 15°C. It seems that at the lower energy levels represented by these tests the effects of declining temperature are not as pronounced as in the previous tests. For example, in the shaker tests (Section 2.3) at 20°C Brand S was effective on fresh J-34 oil at 1:20,000 at 20°C but not at 10°C. The concentration had to be increased to 1:5000 to be effective at the lower temperature. In the hoop tank tests (Section 3.3) Brand S was marginally effective on fresh J-34 oil at 1:10,000 at 20°C; the concentrations had to be increased to 1:5000 at 10°C to be effective. At these concentrations the oil totally dispersed. In the wind-wave tank at 15°C and 10°C there was little difference between dosages of 1:10,000, 1:5000 and 1:1000.

FIGURE 36: EMULSIFICATION VS TIME (J-34)



At constant temperature, as the energy level increased the inhibitor became more effective; its action probably simply enhanced the rate of collision and coalescence of water drops. At constant mixing speed, inhibitor effectiveness declined with declining temperature, probably because the increased oil viscosity reduced both the collision rate and settling rate of water drops. Reduced temperature (as long as the oil does not cool too much and gel) did not seem to affect the final water content though it did appear to increase emulsion stability through hindered settling of water drops.

Under conditions of low temperatures and low mixing levels, such as the levels available in the wind/wave tank, where emulsification of the chemical-free oil was itself inhibited due to viscous oil and a lack of sufficient energy to produce a mousse which contains small water drops, a small amount of inhibitor became effective in preventing significant water incorporation. Increasing the concentration only slightly improved the situation.

Figures 37 and 38 provide similar results for the tests done at energy level 2 (2 m/s wind against 20 cm waves): very little difference in inhibitor effectiveness at the two temperatures and only a slight increase in effectiveness over an order of magnitude in concentration (1:10,000 reduced the water content from 70 to about 40%, 1:1000 reduced it to about 25%). Comparison of Figure 37 with Figure 35 and Figure 38 with Figure 36 indicates that the inhibitor was generally more effective at the higher energy level; this is consistent with the results in the hoop tank.

Figure 39 shows the effect of inhibitor addition on the emulsification of Alberta Sweet Mixed Blend (ASMB) crude oil. At 10°C the oil formed an emulsion in about one hour, at 15°C it took two to three hours. This, again, illustrates the dependence of emulsification rate on temperature; as the oil became more viscous (above the temperature at which it gels) emulsification proceeded faster.

FIGURE 37: EMULSIFICATION VS TIME (J-34)

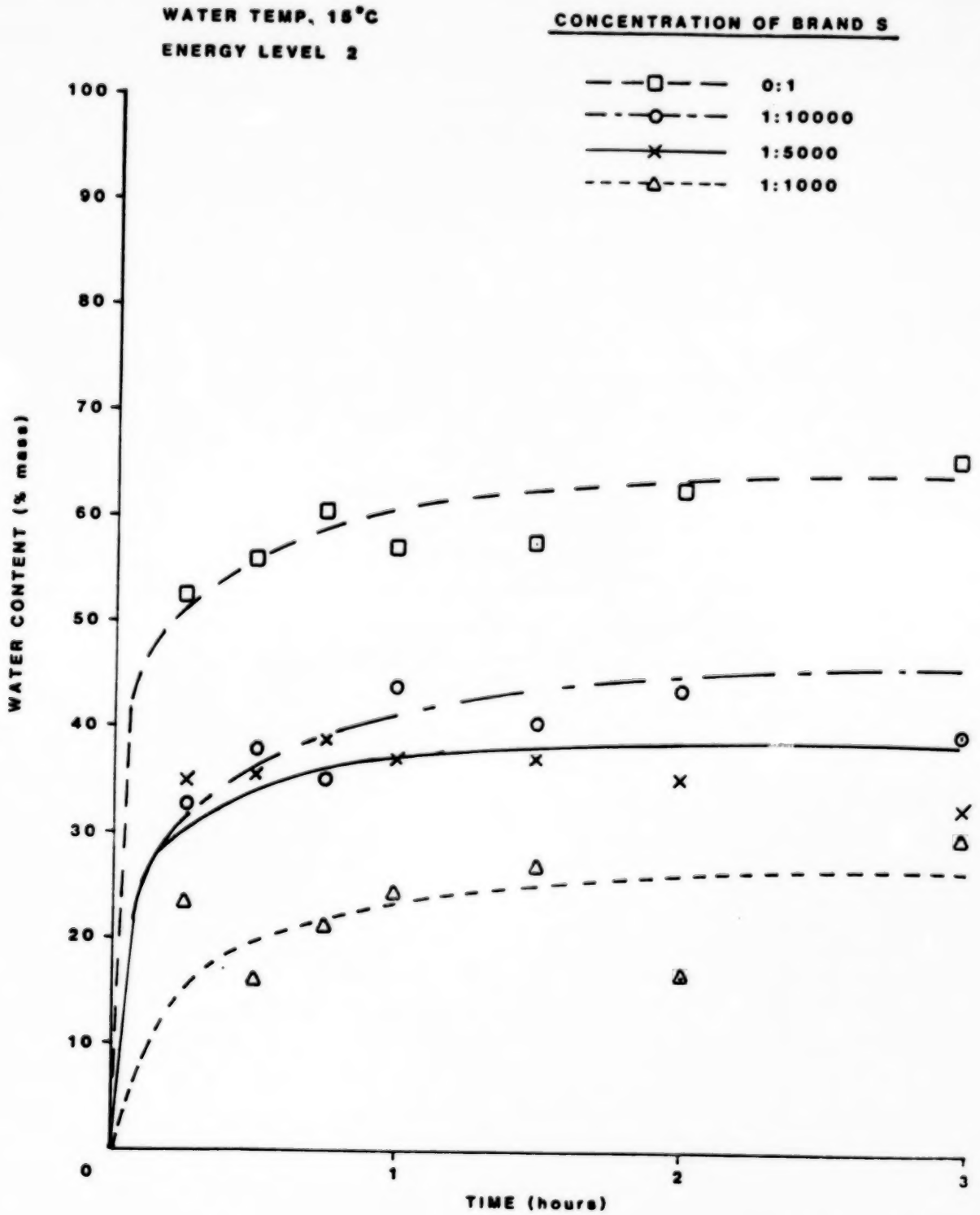


FIGURE 38: EMULSIFICATION VS TIME (J-34)

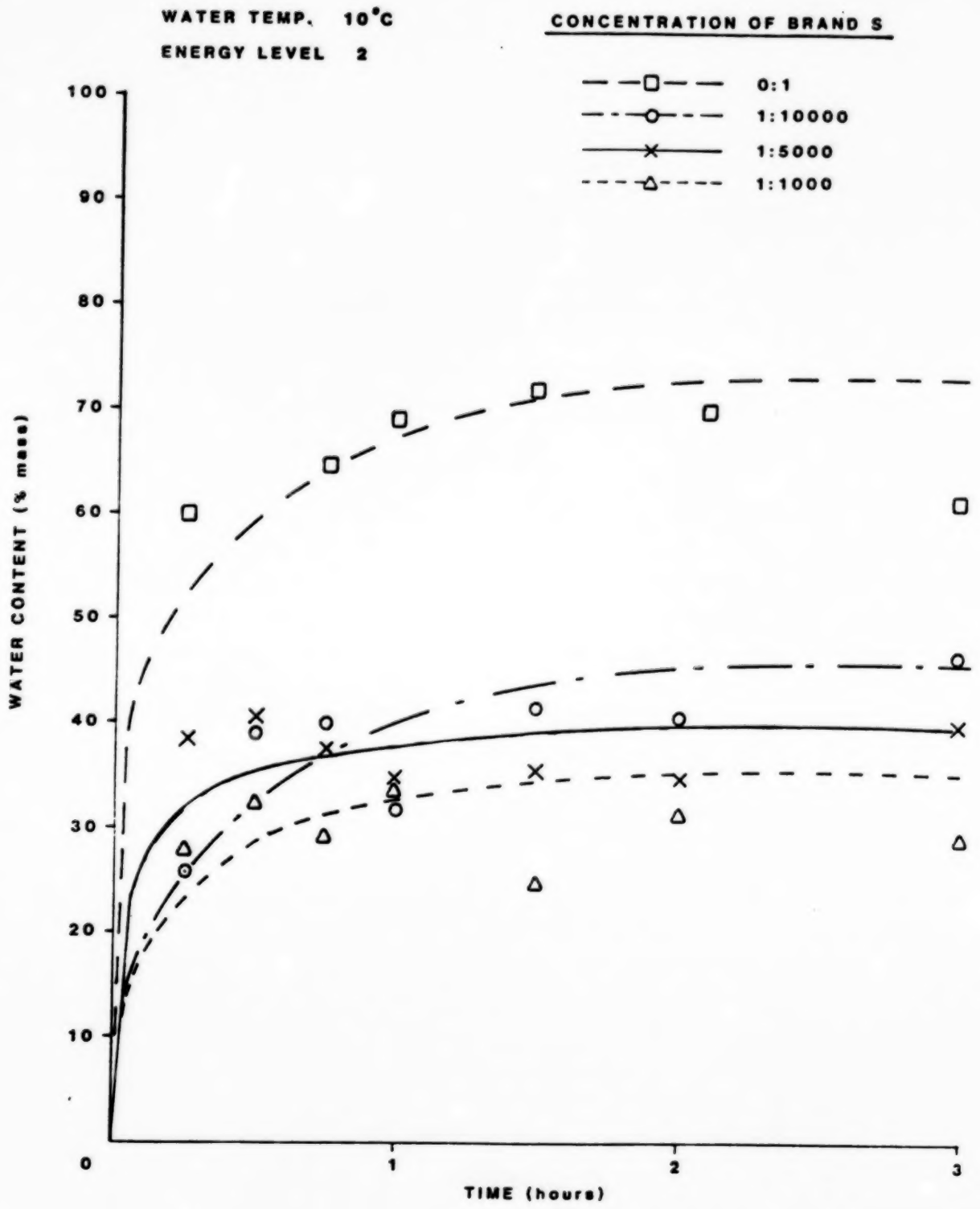
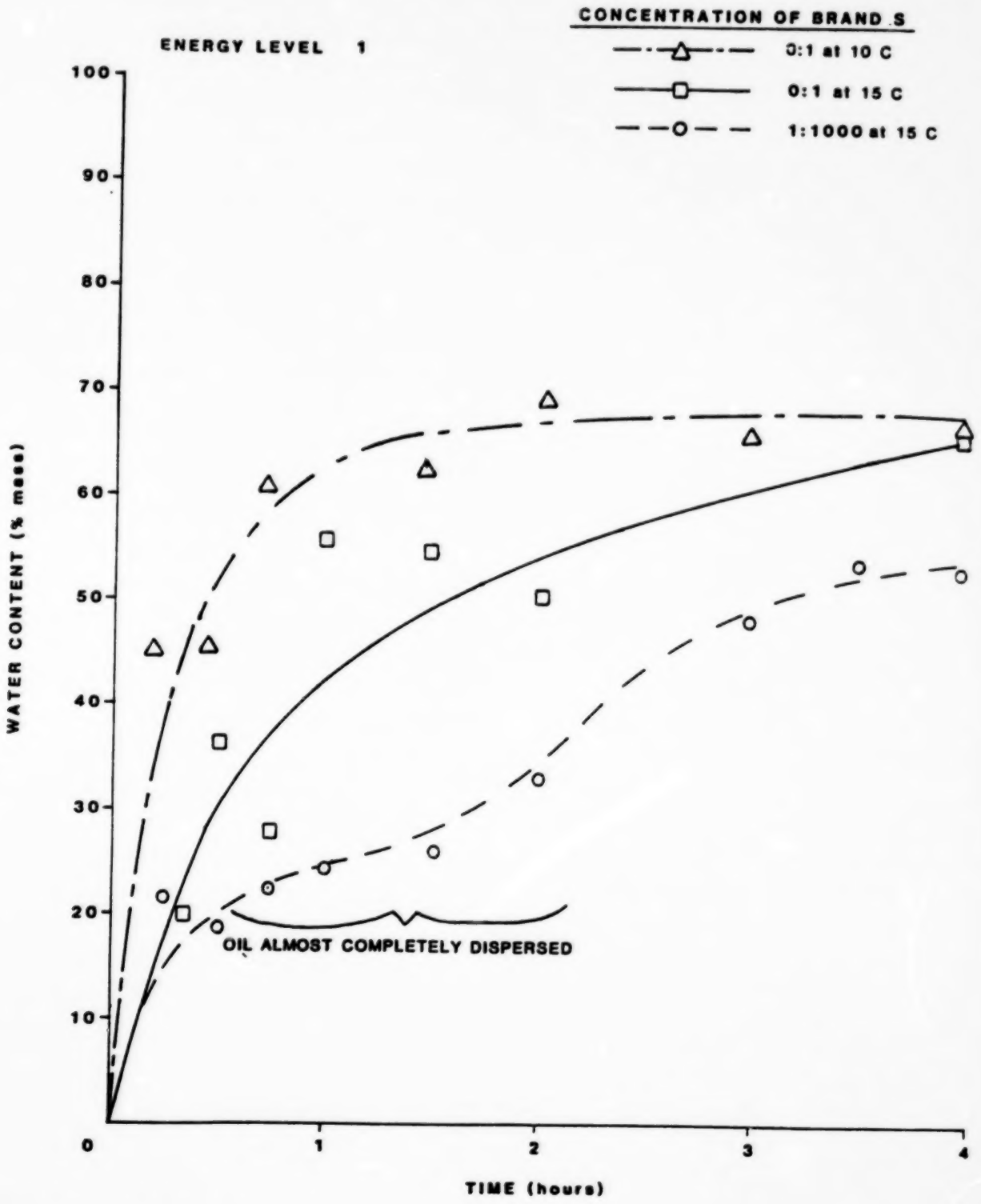


FIGURE 39: EMULSIFICATION VS TIME (ASMB)



At an inhibitor dose of 1:1000 the oil almost completely dispersed over a period of two hours (Figure 40). Dispersed oil concentrations reached about 250 ppm for 1.5 hours. A concentration of 200 ppm represents complete dispersion throughout the entire tank. After 2 hours there was very little of the original 2 L of oil left on the surface, in fact, barely enough to sample. However, after 4 hours much of the dispersed oil had resurfaced and coalesced to form a slick with a water content of about 50%. One explanation for this is that significant leaching of the inhibitor into the water phase occurred because of the much greater interfacial area for mass transfer created by the dispersion process itself.

Figure 41 shows the results of 24-hour tests with the ASMB and J-34 oils. For the ASMB case the oil virtually completely dispersed with peak concentations of 250 ppm (see Figure 40). The oil, after 24 hours, though weathered, still had not formed a "mousse". For the J-34 case, virtually no dispersion of the dosed slick took place and the inhibitor retained its effectiveness for the entire test. The final water content was about 50% and the oil was in the form of small, thick droplets about 25 mm in diameter. In the undosed case the oil had formed a thick, 75% water emulsion in 2 hours. It seems that, if the inhibitor does not greatly enhance dispersion (as it did with the ASMB oil), it stays with the oil for long times and prevents the formation of stable emulsions.

5.4 SUMMARY AND CONCLUSIONS

This phase of the testing showed that Brand S effectively inhibits emulsification in simulated low sea state conditions as well as at high mixing energies. At the lower energy levels (17 to 20 cm waves, 1 to 2 m/s winds) the effects of declining temperature are not as pronounced as in the smaller-scale tests and the effects of increased inhibitor dose are not as dramatic.

FIGURE 40: DISPERSION VS TIME (ASMB)

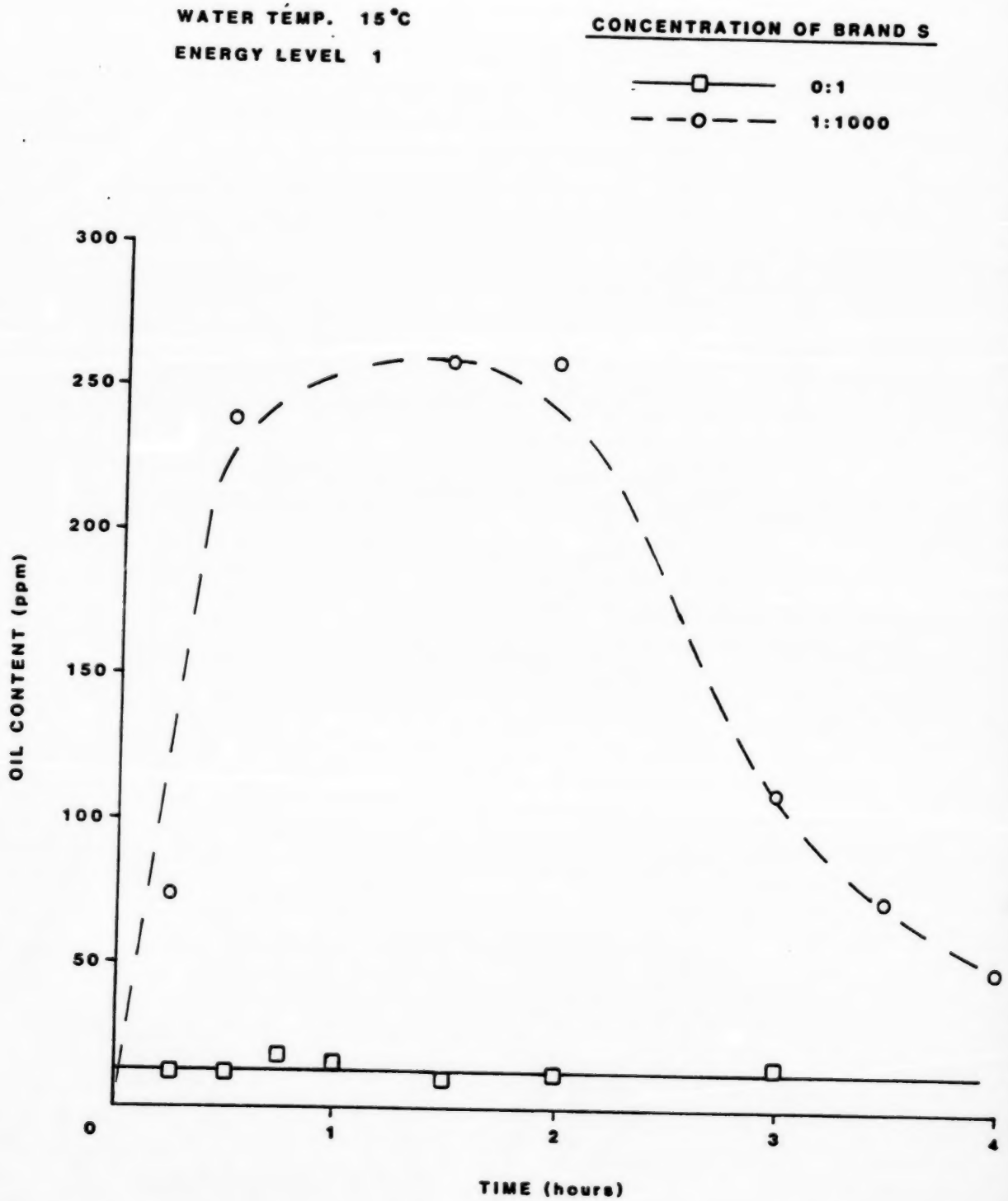
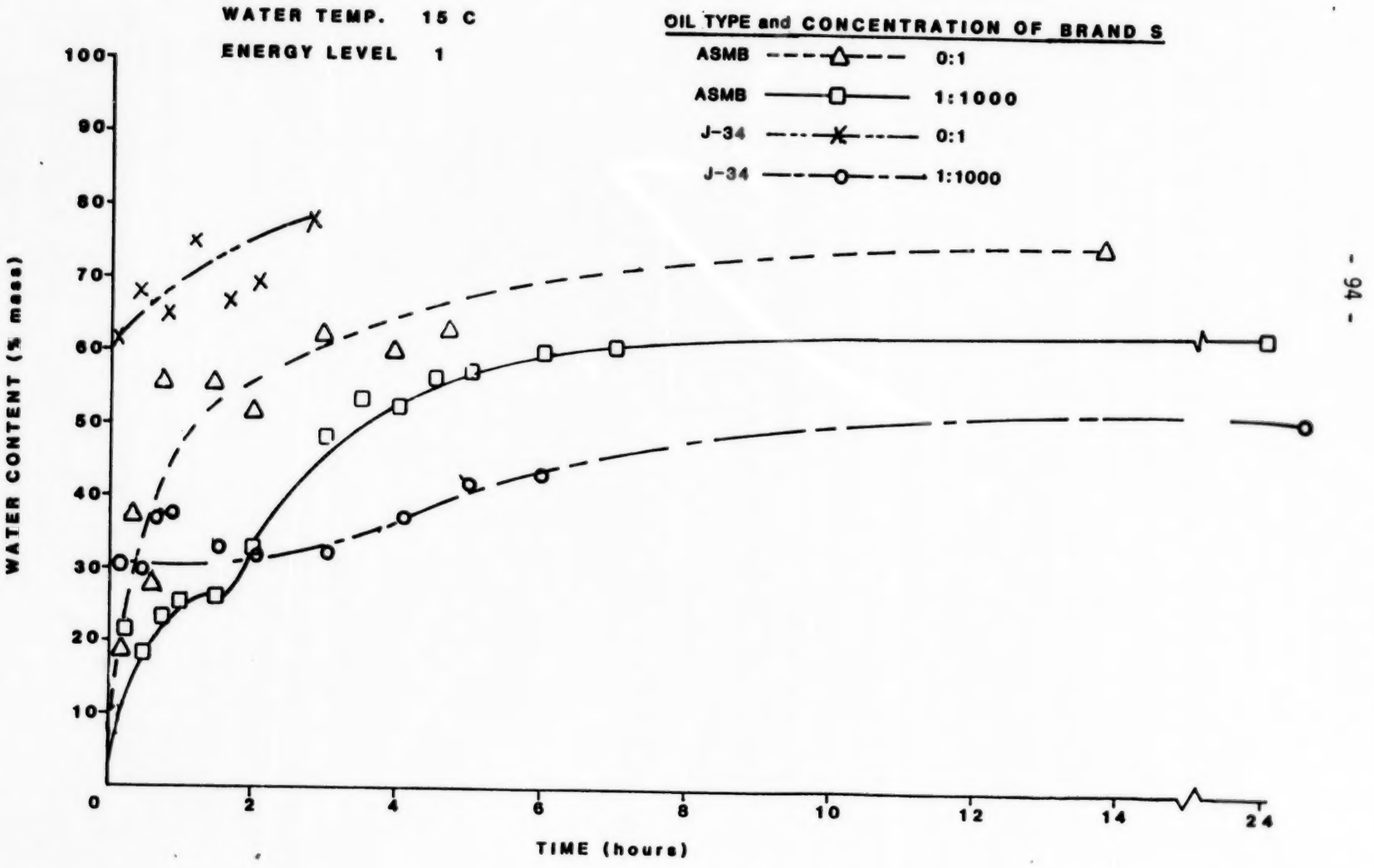


FIGURE 41: EMULSIFICATION VS TIME



When the inhibitor was added to the ASMB oil it completely dispersed, although the chemical may have thereafter leached out of the oil over a two or three hour period. When the inhibitor was added to the J-34 oil, rapid dispersion did not occur but the chemical remained with the oil to prevent the process of emulsification. In either case the effect was advantageous in terms of dealing with oil spills at sea. In the former case the oil will rapidly disperse at sea and will unlikely resurface to form an emulsifiable slick; in the latter case, rapid dispersion will not occur but gradual dispersion will be allowed to proceed because the surface oil's tendency to form a viscous emulsion will have been curtailed.

6.0 MODELLING

6.1 PURPOSE

The intention of this part of the project was to construct a mathematical model linking the processes of emulsification and dispersion and incorporating oil factors and inhibitor dose to permit a complete description of the competition between emulsification and dispersion and the effect of inhibitor addition on various oil types under a wide range of conditions.

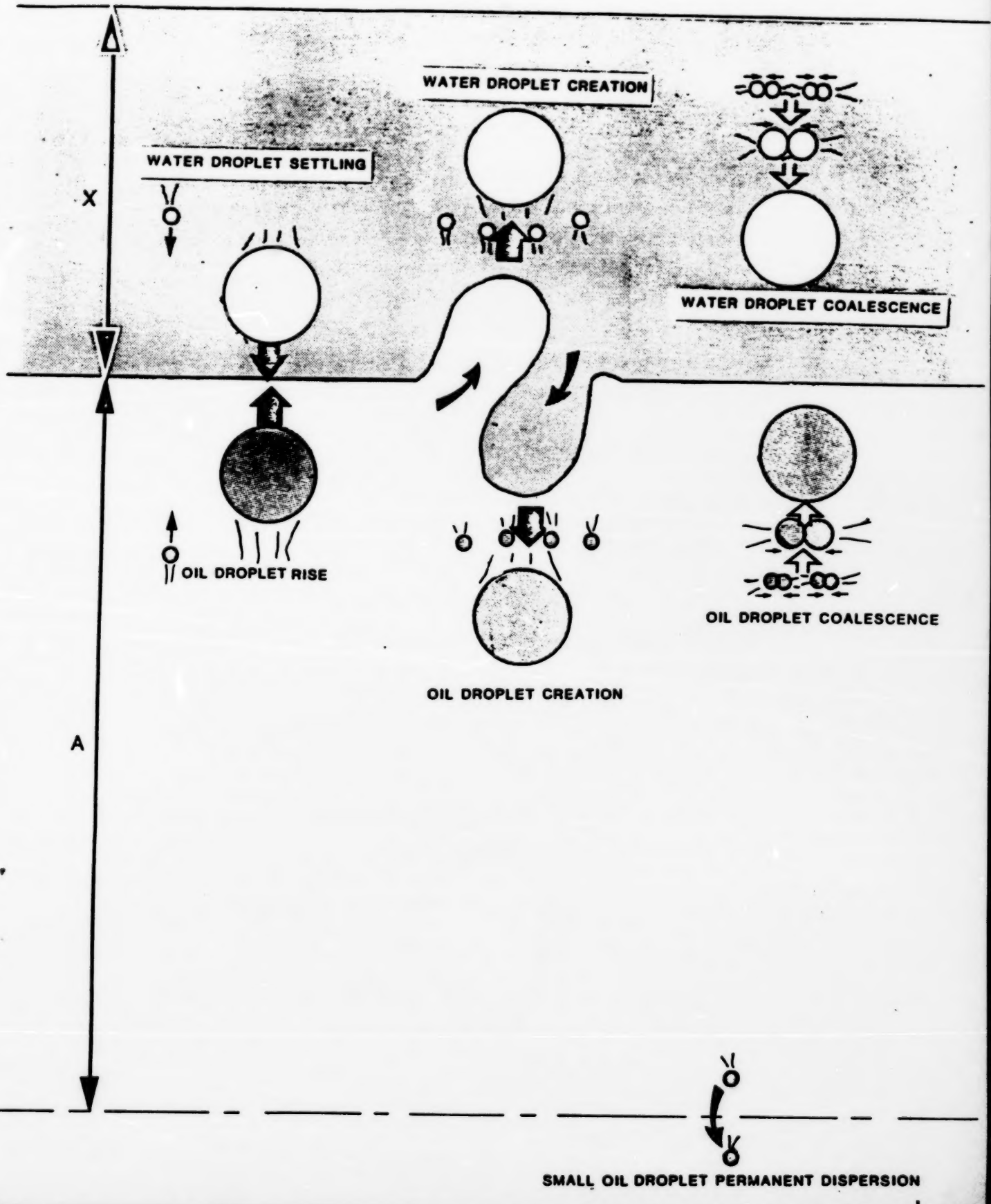
6.2 THEORY

The basis for the model is the work of Mackay and Zagorski (1982) on emulsification and the study of natural dispersion by Buist (1979). The various model processes discussed below are shown on Figure 42.

6.2.1 Emulsification

Emulsification can be viewed as a process in which, as a result of mixing, water droplets of various sizes enter the oil slick at some rate determined by oil properties, oil/water interfacial tension and energy. These droplets, once in the oil, begin to settle out under the influence of gravity, at a rate governed by their size, their relative density to oil and the oil viscosity. Because the oil slick is constantly being mixed, water droplets are constantly colliding within the oil. Depending on the presence and concentration of natural surfactants (thought to be waxes and asphaltenes) these droplet collisions may or may not result in coalescence of the drops. If the collision does end in coalescence the resultant drop will settle out of the oil much faster than the two parent drops. The rate of emulsification is thus the difference between the rate of droplet creation (or water uptake) and the rate of droplet settling (or water release). Written mathematically this is:

FIGURE 42 SCHEMATIC OF MODEL PROCESSES



1) $$\frac{dW}{dt} = R_u - R_s$$

In order to model the emulsification process with sufficient complexity to describe real phenomenon it is necessary to divide the water droplets into two categories, small and large. Small droplets have small settling velocities and large droplets have large settling velocities. Differential equations for both sizes can be written as (Mackay and Zagorski 1982):

2) $$\frac{dW_L}{dt} = F_W K_F (W_M - W_T) - K_{LS} W_L + K_{sc} W_S$$

3) $$\frac{dW_s}{dt} = (1-F_W) K_F (W_M - W_T) - K_{SS} W_S - K_{SC} W_S$$

4) $$\frac{dW_T}{dt} = \frac{dW_L}{dt} + \frac{dW_S}{dt}$$

where W_T, W_N, W_L & W_S = water content of emulsion expressed as the volume ratio of water to oil for total, maximum, large drops and small drops respectively

F_W = fraction of water droplets that are large (i.e., 1 mm diameter)

K_F = rate constant for water droplet formation [s^{-1}]

K_{LS}, K_{SS} = rate constant for settling of large and small droplets respectively [s^{-1}]

K_{SC} = rate constant for coalescence of small droplets into large [s^{-1}]

Analytical solutions, with various boundary conditions, for these equations are given by Mackay and Zagorski (1982), however, for our purposes we need the finite difference forms:

5) $\Delta W_L = \Delta t\,(K_F\, F_W\, (W_M - W_T) - K_S\, W_L + K_{SC}\, W_S)$

6) $\Delta W_S = \Delta t\,(K_F\, (1-F_W)\, (W_M - W_T) - K_{SS}\, W_S - K_{SC}\, W_S)$

7) $\Delta W_T = \Delta W_L + \Delta W_S$

6.2.2 Dispersion

Using a modification of the approach proposed by Buist (1979), similar equations for natural dispersion can be written as:

8) $\frac{dO_L}{dt} = F_O R_F - K^1_{LR} O_L + K^1_{SC} O_S - R_{PDL}$

9) $\frac{dO_S}{dt} = (1 - F_O)\, R_F - K^1_{SR}\, O_S - K^1_{SC}\, O_S - R_{PDS}$

10) $\frac{dO_T}{dt} = \frac{dO_L}{dt} + \frac{dO_S}{dt}$

where O_T, O_L, O_S = volume ratio of oil to water in a well mixed zone of depth A

F_O = fraction of oil droplets that are large (i.e., 1 mm)

R_F = rate of formation of oil droplets [s^{-1}]

K^1_{LR}, K^1_{SR} = rate constant for rising of large and small droplets respectively [s^{-1}]

K^1_{SC} = rate constant for coalescence of small oil droplets [s^{-1}]

R_{PDL}, R_{PDS} = rate of diffusion of large and small droplets respectively into the water column [s^{-1}].

Several assumptions can be made to simplify these equations:

a) since oil concentrations are very low beneath a slick and thus the droplets are widely separated, $K^1_{SC} \cong 0$

b) since large oil droplets have large rising velocities and are unlikely to diffuse away from the slick before they resurface, $R_{PDL} \cong 0$ and, in laboratory apparati $R_{PDS} = 0$

Thus, in finite difference form:

11) $\Delta O_L = \Delta t\ (F_O\ R_F - K^1_{LR}\ O_L)$

12) $\Delta O_S = \Delta t\ ((1 - F_O)\ R_F - K^1_{SR} - R_{PDS})$

13) $\Delta O_T = \Delta O_L + O_S$

6.2.3 Linking the Models

The emulsification and dispersion models are linked by a mass balance on the oil slick, which in terms of slick thickness can be written as:

14) $X = (W_T + 1)\ (X_O - O_T\ A)$

where X_O, X = initial and final slick thickness [m]

A = depth of well mixed layer beneath slick [m]

6.2.4 Rate Constant Expressions

Figure 42 illustrates the various physical processes thought to be taking place in an oil slick on water in the presence of mixing energy.

6.2.4.1 K^1_F and K_F

Buist (1979) developed expressions for the rate of oil droplet generation by breaking and non breaking waves. Taking the case of the breaking waves:

15) $K^1_F = f/2P$ where

f = fraction of sea surface covered by breaking waves

P = wave period (s)

or, in an artificially mixed system by dimension reasoning:

16) $K^1_F = CW$

where C = constant

W = frequency of mixer [s^{-1}]

For each unit of energy put into the oil/water system a certain amount of interfacial area, controlled by the interfacial tension and phase viscosities, is created. It is not possible, with our present state of knowledge, to predict what fraction of the interfacial area is oil droplets in water and the remainder water droplets in oil. As a first approximation for modelling purposes it will be assumed that:

17) $K_F = m K^1_F$

where m is a constant that may be some function of phase properties.

6.2.4.2 F_O and F_W

Buist (1979) developed an expression of the fraction of oil droplet larger than 100 um diameter created by breaking waves:

18) $F_O = 1 - 1.9 \times 10^{-5} X^{-1} (24/\sigma_o) (10/\mu_o)^2 (A/0.15)/(1 + 1.9 \times 10^{-5} X^{-1})$

where σ_o =oil/water interfacial tension (mN/m)

μ_0 = oil viscosity (mPas)

A = wave height (m)

By analogy, it seems reasonable that, since viscosity is the only factor in equation 18 that differs between oil and water

19) $F_W = 1 - N \mu_o/\mu_w (1 - F_o)$

where N = a constant

This implies that, for a given energy input that the fraction of water droplets in oil that are small is greater than the fraction of oil droplets in water that are small.

6.2.4.3 K^1_{LR} and K^1_{SR}

The rate constant for the rising of oil droplets through the water (assuming this controls the process of droplets rejoining the slick and not the rate at which droplets coalesce with the slick) is related to the Stokes rise velocity divided by a length scale (assumed to be the mixing depth or wave height (A), which for a 100 μm diameter oil droplet in seawater is:

20) $K^1_{SR} = 1.6 \times 10^{-3} / A$

and, for a 1 mm drop is:

21) $K^1_{LR} = 1.6 \times 10^{-1} / A$

6.2.4.4 K_{LS} and K_{SS}

The rate constant for the settling of water droplets through oil (assuming this controls the rate and not recoalescence of water droplets with the underlying water) is related to the Stokes fall velocity divided by a length scale (assumed to be the slick thickness). For a 100 um diameter water droplet in oil:

22) $K_{SS} = 5.6 \times 10^{-8} (\rho_w - \rho_o)/\mu_o X$

and, for a 1 mm diameter water droplet:

23) $K_{LS} = 5.6 \times 10^{-6} (\rho_w - \rho_o)/\mu_o X$

6.2.4.5 K_{SC}

The rate constant for coalescence of small water droplets is related to fluid factors (number of droplets, density and viscosity) mixing factors (frequency and characteristic length) and oil factors (the stability coefficient, containing wax content, asphaltene content and temperature).

Mackay and Zagorski (1982) suggested the following for K_{SC}:

24) $K_{SC} = C/S^5$

where S = stability coefficient for oil

C = a function of fluid and mixing characteristics [s^{-1}]

and

25) $S = C_A \exp(-0.045\,(T-293)) \exp(3.3\,(1-C_A - C_W)^2 + 200\,C_W^{\,2})$

where T = temperature (^oK)

C_A = mass fraction ashpaltenes

C_W = mass fraction waxes

Dimensional analysis leads us to postulate that C has the form:

26) $C = B\ W^2\ L^2\ W_T/\mu o$

where B is a constant

Since it is believed that addition of the inhibitor only enhances the probability of successful coalescence of two colliding water droplets it seems appropriate to include the effect in the expression for K_{SC}. Since the stability coefficient, S, is related to the ability of stabilizing compounds in the oil to prevent successful coalescence, the expression for inhibitor addition must override this; an appropriate one is:

27) $C = F(\exp PC_I^{\,Q})$

where C_I = volume fraction of inhibitor

P, Q = constants

The final form of the equation for K_{SC} is thus:

28) $K_{SC} = B \ W^2 L^2 W_T \exp PC_I \ ^O/S^5 \mu o$

6.2.5 Property Changes

For the purposes of this model only changes in oil viscosity due to water uptake and oil/water interfacial tension due to inhibiter addition are included. Other property changes due to oil weathering could easily be added, if required, using the evaporative exposure technique of Stiver and Mackay (1983) and subsequent property change equations proposed by Mackay et al 1983.

6.2.5.1 Viscosity

The change in viscosity associated with water uptake is correlated using the adaptation of the Mooney equation proposed by Mackay and Zagorski (1983) (see also Figure 7):

29) $\mu = \mu_o \exp ((2.5 \ W_T/(W_T + 1))/(1-(0.65 \ W_T/(W_T + 1))))$

6.2.5.2 Interfacial Tension

The effect of inhibiter addition on oil/water interfacial tension is modelled using data obtained with a duNuoy ring apparatus. The relationship is:

30) $\sigma = \sigma_o (9.43 - (8.43T/293)) \exp (- 13 \ C_I \ ^{0.3})$

6.3 MODEL RESULTS

A computer program listing may be found in Appendix I.

Approximate values for the constants in the previous section were found to be:

Equation 16 - $C = 1.4 \times 10^{-5}$

Equation 17 - $m = 20$

Equation 19 - $N = 4$

Equation 28 - $B = 7 \times 10^{-5}$

$P = 10^{3}$

$Q = 0.6$

An example of the model results are shown in Figures 43 and 44. With no inhibitor present the oil rapidly emulsifies to about 75% of which about 40% is in the form of small droplets. The oil disperses to a concentration of about 65 ppm. At an inhibitor dose of 1:10,000 the total water content and dispersion are only slightly affected. The major change is in the small water content which drops to about 10%. At 1:5,000 both total and small water content are greatly reduced and dispersion is increased to 230 ppm. At 1:1,000 the oil completely disperses in 15 minutes.

Areas for further refinement in the model include the relationship between the rate of oil and water drop production, the size distribution of oil and water drops produced and the effect of small and large water drops on emulsion viscosity.

FIGURE 43
MODEL RESULTS - EMULSIFICATION versus TIME

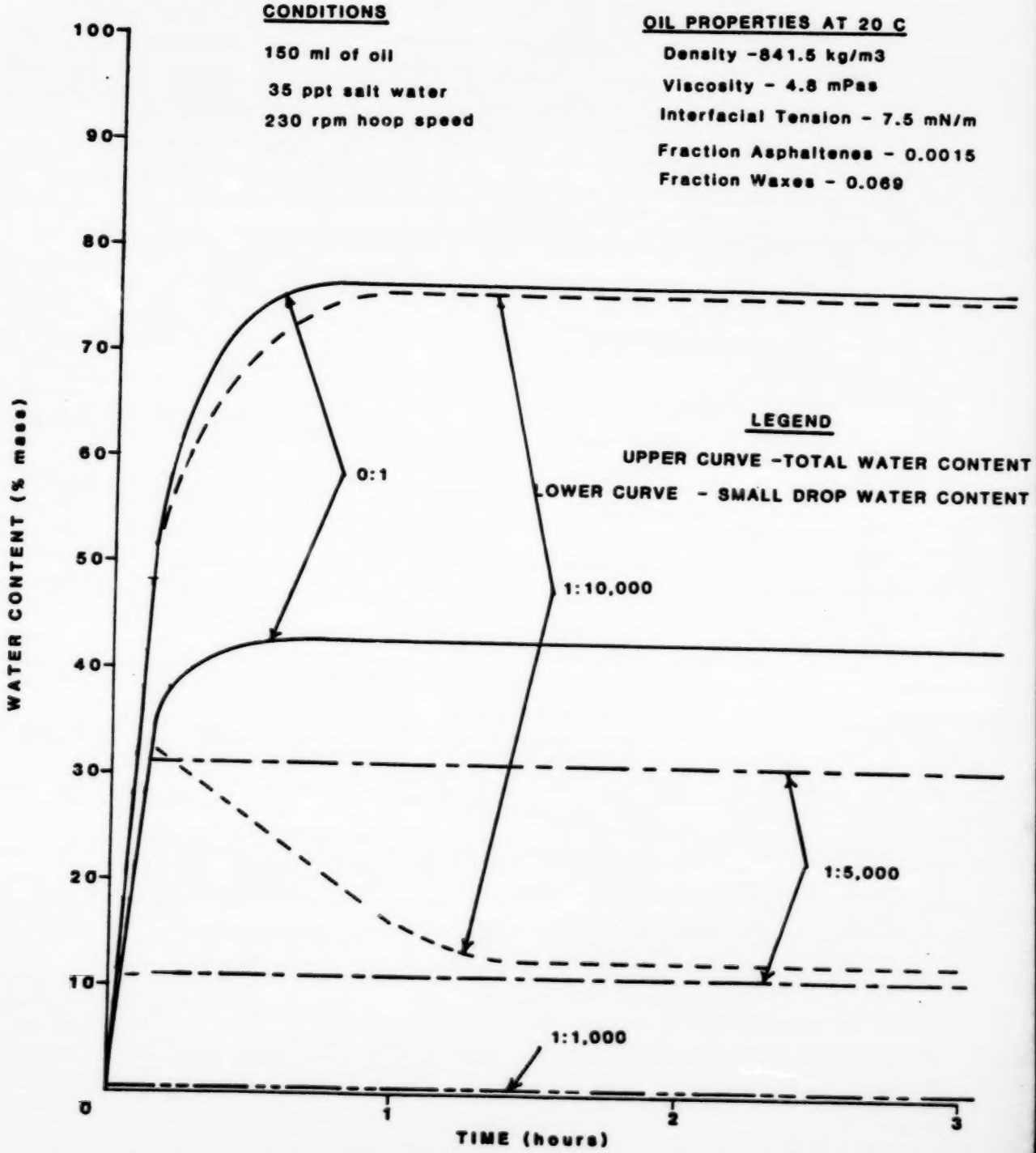


FIGURE 44
MODEL RESULTS - DISPERSION versus TIME

CONDITIONS

150 ml of oil

35 ppt salt water

230 rpm hoop speed

OIL PROPERTIES AT 20 C

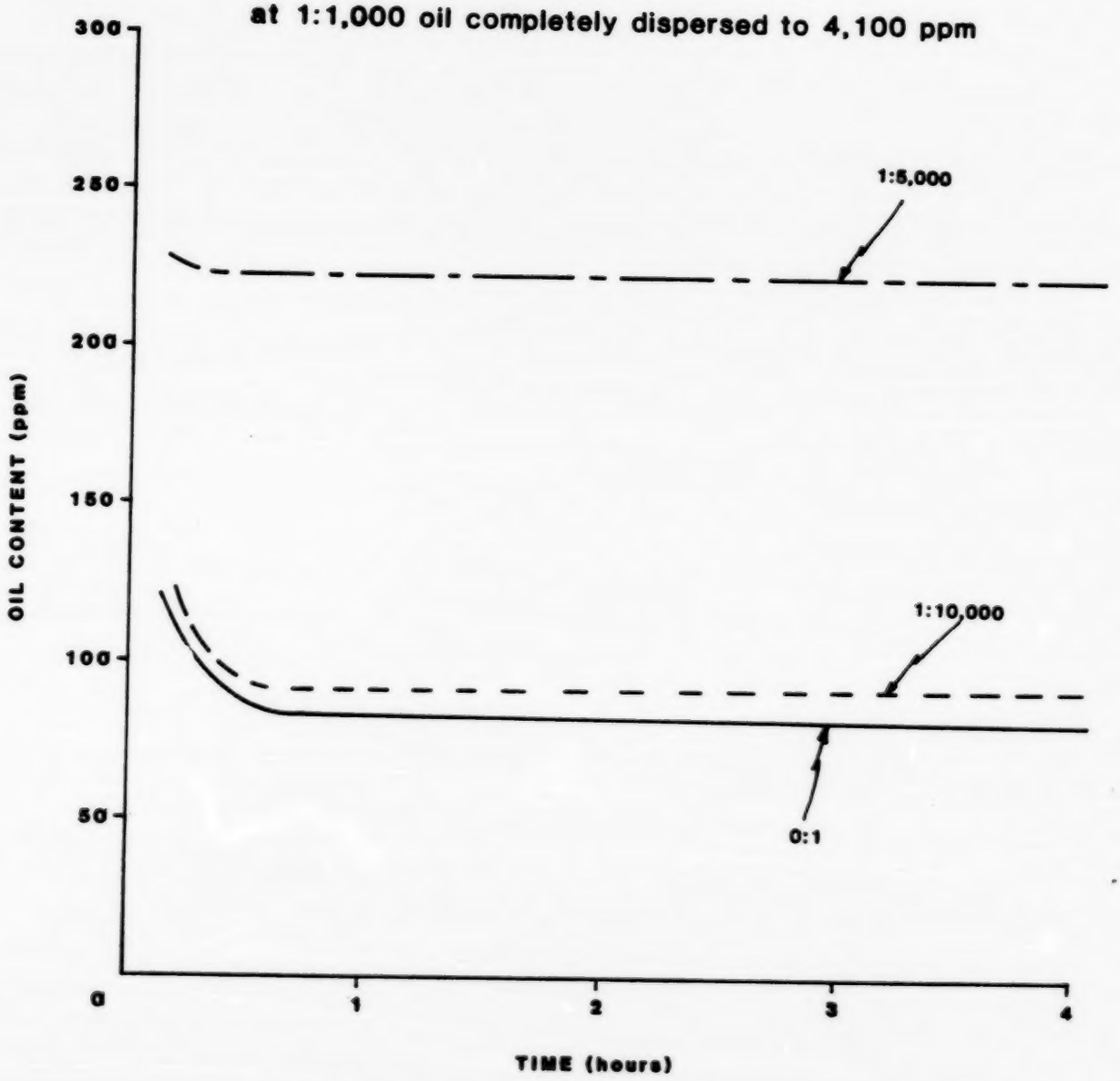
Density -841.5 kg/m3

Viscosity - 4.8 mPas

Interfacial Tension - 7.5 mN/m

Fraction Asphaltenes - 0.0015

Fraction Waxes - 0.069



7.0 CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

* Of the emulsion inhibiting surfactants tested, Brand "S" showed the most promise because of its performance in both preventing emulsification and promoting dispersion at low dosages and its very high oil/water partition coefficient.

* A dose rate of 1 part Brand "S" in 20,000 parts oil was the minimum required to inhibit emulsification with fresh crude oil at 20°C. Increased oil viscosity through either evaporation or cooling require higher dosages, up to 1:1,000 at 0°C for fresh oil.

* If the treated or untreated oil is at a temperature about 20°C below its pour point no emulsification occurs; the oil forms into smooth balls of semi-solid oil.

* Brand "S", in addition to effectively inhibiting emulsification, also dramatically promotes dispersion of oil at temperatures above 10°C and at dosages in the range of 1:1,000. The presence of the inhibitor slightly enhances the effectiveness of conventional chemical dispersants.

* Four regimes of emulsion prevention have been identified. First, with no inhibitor present, the oil (unless 20°C below its pour point) rapidly takes up water to form a stable, highly viscous brown emulsion (a "mousse"). Second at certain low concentrations of inhibitor, the oil still emulsifies but the emulsion is black coloured and the entrained water droplets are larger and the water content, viscosity and stability of the emulsion are lower than with the inhibitor-free oil. Third, at higher inhibitor concentrations, emulsification is prevented and the oil remains fluid. At this stage dispersed oil concentrations are higher than for the untreated oil. Finally, at still higher inhibitor concentrations the oil is completely dispersed into the water in the form of very small droplets.

* An oil slick, dosed with the appropriate concentration of inhibitor, will, over long time periods, do one of two things; it will either rapidly disperse or not emulsify and disperse more slowly, but at a rate much faster than untreated emulsion. In either case the effect is advantageous from the perspective of spill cleanup and impact.

* Increased levels of mixing energy enhance the effect of the inhibitor.

* Brand "S" is most effective when premixed with the oil. Dropwise addition using toluene as a solvent is only slightly less effective then premixed.

* The action of the inhibitor is twofold. First, it seems to greatly enhance the rate at which small water droplets in the oil coalesce to form larger, faster settling water drops. This is likely due to the inhibitor molecules replacing or counteracting the naturally occurring surfactants in the oil that prevent water droplet collisions from resulting in coalescence. Second, the inhibitor reduces oil/water interfacial tension thus promoting dispersion of the oil.

A mathematical model has been developed which describes and links the processes of emulsification and dispersion as a function of oil properties and makeup, mixing energy and inhibitor dose.

7.2 RECOMMENDATIONS

* A small-scale field trial of the inhibitor product is recommended.

* Further work on the effects of the inhibitor by sprayed application onto fresh, weathered and emulsified oils in the wind/wave tank is recommended.

* Further study to elucidate the mechanisms of emulsion formation, particularly in non-breaking wave conditions, is recommended.

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APPENDIX I

COMPUTER PROGRAM LISTING

```
      PROGRAM EANDD
      REAL INTI,INT,KSS,KF,KLS,KSC,L,N
      OPEN(2,FILE=''_PT1:')

C     INITIALIZE

      II=0.0
      TCHECK=0.0
      T=0.0
      WT=0 0
      WL=0.0
      WS=0.0
      OT=0.0
      OL=0.0
      OS=0.0

C     READ RUN DATA

      OPEN (9,FILE='EANDD.DAT')
      READ(9,100)INTI
      READ(9,100)DEN
      READ(9,100)VIS
      READ(9,100)X
      READ(9,100)CA
      READ(9,100)CW
      READ(9,100)CI
      READ(9,100)TEMP
      READ(9,100)PWCM
      READ(9,100)AMP
      READ(9,100)FREQ
      READ(9,100)TIMEM
      READ(9,100)DT
      READ(9,100)TOUT
      READ(9,100)L
      READ(9,100)C
      READ(9,100)N
      READ(9,100)P
      READ(9,100)Q
      READ(9,100)B
      READ(9,100)A
      READ(9,100)D

100   FORMAT(30X,F20.9)

      WRITE(2,100)INTI
      WRITE(2,100)DEN
      WRITE(2,100)VIS
      WRITE(2,100)X
      WRITE(2,100)CA
      WRITE(2,100)CW
      WRITE(2,100)CI
      WRITE(2,100)TEMP
      WRITE(2,100)PWCM
      WRITE(2,100)AMP
```

```
      WRITE(2,100)FREQ
      WRITE(2,100)TIMEM
      WRITE(2,100)DT
      WRITE(2,100)TOUT
      WRITE(2,100)L
      WRITE(2,100)C
      WRITE(2,100 N
      WRITE(2,100)P
      WRITE(2,100)Q
      WRITE(2,100)B
      WRITE(2,100)A
      WRITE(2,100)D

      WM=PWCM/(100-PWCM)
      XO=X
      VISO=VIS

C *   INITIAL INTERFACIAL TENSION

      INT=INTI*(9.43-8.43*TEMP/293.)*(EXP(-13*CI**0.3))

C *   RATE : DROP PRODUCTION

1     KF=C*FREQ
      RF=A*KF

C   LARGE DROP FORMATION
133   FORMAT(2X,3(F15.5,2X))
      FOS=(1.9E-05/X)*(24/INT)*(10/VIS)*(AMP/0.15)
      FWS=N*(VIS/10.0)*FOS
      IF(FOS.GT.1.0)FOS=1.0
      IF(FWS.GT.1.0)FWS=1.0
      FO=1-FOS
      FW=1-FWS

C   RATE : SMALL DROP RESURFACING

      RSS=1.6E-03/AMP

C   RATE : LARGE DROP RESURFACING

      RLS=0.16/AMP

C   RATE : SMALL WATER DROP SETTLING
      KSS=D*(1023.5-DEN)/(X*VISO)

C   RATE : LARGE WATER DROP SETTLING

      KLS=1E02*KSS*(VISO/VIS)

C   STABILITY COEFF FOR OIL

      S=CA*EXP(-0.045*(TEMP-293))*EXP(3.3*(1-CA-CW)**2+200*CW*CW)
C   RATE : SMALL WATER DROP COAL.
      KSC=(B*DEN*FREQ*FREQ*L*L*WT*EXP(F*CI**Q))/(S**5*VIS)
```

```
C  RATE : PERMANENT DISPERSION

         RPD=0.0

C CALC WATER CONTENT PARAMETERS

         DWL=DT*(FW*KF*(WM-WT)-KLS*WL+KSC*WS)
         DWS=DT*((1-FW)*KF*(WM-WT)-KSC*WS-KSS*WS)
         IF((DWS+WS).LT.0.0) THEN
         DWS=0.0
         DWL=0.0
         ENDIF
         DWT=DWL+DWS
         WT=WT+DWT
         WL=WL+DWL
         WS=WS+DWS
         PWT=WT/(WT+1)*100
         PWS=WS/(WS+1)*100
         PWL=WL/(WL+1)*100

C  CALC OIL DROP PARAMETERS
         DOL=DT*(FO*RF-RLS*OL)*(1-(WT/(WT+1)))
         DOS=DT*((1-FO)*RF-RSS*OS-RPD)*(1-(WT/(WT+1)))
         DOT=DOL+DOS
         OS=OS+DOS
         OT=OT+DOT
         OL=OL+DOL
         PPMOT=1E06*OT/(OT+1)
         PPMOL=1E06*OL/(OL+1)
         PPMOS=1E06*OS/(OS+1)

C   CALC NEW OIL THICKNESS
         X=(WT+1)*(XO-OT*AMP*6.0)

C  CALC NEW VISCOSITY

         VIS=VISO*EXP(0.025*PWT/(1-0.0065*PWT))


C ITERATE TIME
         TCHECK=TCHECK+DT
         T=T+DT
         ET=T/60

         IF(TCHECK.LT.TOUT) GO TO 999
         TCHECK=0.0
C  OUTPUT

199      WRITE(2,200)ET,PWT,PWS,PPMOT,PPMOS,X,VIS,FW

200      FORMAT(2X,/,/,
     +40X,'ELAPSED TIME      ',F20.9,/
     +5X,'TOTAL WATER CONT   ',F20.9,/,
     +5X,'SMALL WATER CONT   ',F20.9,/,
```

```
     +5X,'TOTAL OIL CONC     ',F20.9,/,
     +5X,'SMALL OIL CONC     ',F20.9,/,
     +5X,'SLICK THICKNESS    ',F20.9,/,
     +5X,'OIL VISCOSITY      ',F20.9,/,
     +5X,'LARGE DROP FRAC    ',F20.9,/,)
        IF(II.EQ.1) GO TO 999

888     IF(X.LE.1E-05 .OR. T.GE.TIMEM) THEN
        II=1
        GO TO 199
        ELSE
        GO TO 1
        ENDIF
999     STOP
        END
```